AB INITIO CALCULATIONS ON SOME MOLECULE IONS

by

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Abstract

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Ground state Hartree-Fock-Roothaan calculations, using Gaussian basis sets, have been done on several open and closed shell molecular ions. These are all positive ions which contain a positive core surrounded by one or more neutral species. Calculations are reported on the hydrogen cluster ions H_n^+, with n an odd number between three and fifteen. Geometries and binding energies are reported for these systems with particular emphasis on H_{11}^+. The ions $Be^{2+}He$, Be^+He and $B^{2+}He_2$ are also discussed. These have all been predicted to be stable and bond lengths and binding energies are reported. The calculations on the ion $Be^{2+}He$ have been extended to short internuclear separations (0.16 to 0.79Å) and the implications of these results for the low energy ($\lesssim$ 1000eV) scattering of Be^{2+} ions by He atoms is considered. Other systems studied include He_3^{2+} and He^{2+} and $He^{2+}(H_2)_2$, both of which are predicted to be unstable, and HeC^{2+} and HeC^+. These latter two

ions are predicted to be stable and binding energies, bond lengths and spectroscopic constants are presented for them.

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I

INTRODUCTION

The bonding of neutral molecules or atoms to ions and the calculation of the geometries and energetics of these systems has been the subject of a number of investigations. The term "cluster ion" has been introduced and defined to mean "ions which have a central ionic core to which some molecule(s) is (are) bonded primarily by electrostatic forces."[1] All ions discussed here will be of this type.

Early experimental studies of cluster ions were prompted by Wilson's[2] observations, during the 1890's, of the ion induced condensation of clouds from the gas phase. This has led to studies of ion-induced nucleation which is asserted to be of importance in atmospheric processes, in cloud chambers, to aerosol production in the presence of ionizing radiation and via ion-molecule swtiching reactions.[3-6]

There have been suggestions that ion clusters exist in interstellar clouds[7] and in planetary atmospheres.[1,8] The hydrogen ion clusters H_n^+ have been suggested to be the cause of the absorption and polarization of stellar radia-

tion in interstellar space.[9] This has been challenged,[10] on the ground that interstellar densities are far too low for such processes. Hoyle, and others[11,12] have, however, proposed that the condensation of hydrogen on graphite grains at 3°K might promote the formation of galaxies and stars. Ion clusters could then form by interaction with radiation.[3] It should be noted that the hydrogen clusters H_n^+ have been observed experimentally.[7,13] These have been observed to have all values of n from 1 to 99 with n odd for $n \geq 3$.

It has been proposed that clustering processes in the atmosphere of Venus lead to the formation of coagulates which give rise to the ultraviolet haze layer which has been observed.[8] This clustering is believed to involve clusters of the form $CO_2^+.CO_2$. The complexes $CO_2^+.(H_2O)XY$ can also form as has been observed with NO^+, H_2O and SO_2 systems.[6]

Large clusters of water molecules may play a role in the upper atmosphere.[1,14,15] These clusters have the form $H^+ (H_2O)_n$ and are called hydrated protons. Cluster ions of this type are believed to be formed by a series of reactions with either NO^+ or O_2^+ as the principal precursor ion.

Kinetic studies of proton hydrate equilibria in the gas phase have been done[16,17] and have thrown light on the problem of the solvation of ions. Attachment of water molecules to the hydrogen ion had been observed mass spectro-

metrically, prior to the above work, in flames, [18], field emission,[19] and gas discharges.[20] Clustering of water molecules on alkali metal ions has also been observed.[21,16]

It has been reported that cluster ions of the form $M^{2+}.(X)_n$, where M^{2+} is Mg^{2+}, Ca^{2+}, and Ba^{2+} and X is one of the neutrals Ar, O_2, N_2, CO, and CO_2, N_2O, and H_2O exist and the rates of association of these species have been measured.[22] Also the cluster reaction rates of Na^+ and K^+ have been measured with O_2 and CO_2.[23] The association rates of Cl^- with H_2O and NO_2^- with H_2O have also been measured.[24]

It has already been mentioned that cluster ions of the form H_n^+ exist. These are also written $H^+(H_2)_n$. It is not surprising that clusters of the form $Li^+(H_2)_n$, with n even, have also been observed.[30] Also ions of the form BeH_n^+, with n odd, have been detected.[26]

An interaction similar to those already mentioned. but leading to a bond between a rare gas atom and a metallic ion has been postulated to account for perturbations on the frequencies of rotational and vibrational spectra and changes in geometry when a molecule is trapped in a rare gas matrix (as in matrix isolation spectroscopy).[27] For one molecule, MgF_2, there is evidence that in the matrix it is bent,[28] but in the gas phase it is linear.[29] This may be explained by an interaction between the highly ionic Mg atom and the rare gas matrix. This will be discussed in more detail later.

There is experimental evidence that cluster ions of the form $Li^+(Ne)_n$ with $n \leq 6$ exist.[30] These have been pro-

duced by bombarding solid neon with low energy lithium ions. Earlier work,[31] based on mobility studies, suggests that the ion $Li^+ He_2$ exists. Recently the ion Li^+ (Ar) has been detected in a drift tube.[89]

Very large cluster ions of hydrogen, with m/e ratios up to several thousand have been observed during electron excitation of large neutral hydrogen agglomerates formed in supersonic hydrogen jets.[32] Presumably the larger clusters are Van der Waals aggregations. As previously mentioned small hydrogen cluster ions of the type H_n^+, with n odd, have been produced by excitation of condensed hydrogen layers at 3°K with low energy electrons.[7] It has been reported that a maximum exists at m/e 15. However, other studies indicate a maximum at m/e 9 as well as at 15.[13] The deuterium cluster ions D_n^+ have been reported to exist and D_{11}^+ and D_{15}^+ appear to be the most abundant species.[33]

Mass spectra of ions of the form $K^+(H_2)_n$ have been observed.[33] The ion $K^+(H_2)_{32}$ has been reported to be very prominent and it has been suggested that this ion consists of two shells of 12 and 20 molecules distributed around an icosahedron.[33] It is interesting that the ion $Ar^+(Ar)_{32}$ has been postulated to exist based on arguments from mobility data.[34]

Ions of the form $O_2^+ (O_2)_n$ have been observed experimentally. The values of $\underline{n}$ reported run from n=1 to

8.[36] It has also been suggested that cluster ions of the form $O_2^-(O_2)_n$ exist based on mobility data.[37]

Ions of the type N_n^+ with n=5 to 9 have been produced in a flowing afterglow.[38] Also the ions $O_2^+(N_2)$ and N_4^+ have been reported.[33]

There is evidence for the existence of a number of other ions including ammonia ions such as $NH_4^+(NH_3)_n$ with $n \leq 20$,[39,40] ions of the type $H^+(H_2O)_n(CH_3OH)_m$ (in gaseous water - methanol mixtures),[41] and ions like $O_2^-(H_2O)_n$, $O^-(H_2)_n$, $OH^-(H_2O)_n$, and $NO^-(H_2O)$.[33]

The ions He_n^+ have also been observed with n=1 to 4.[44]

Considerable theoretical work has been done on cluster ions. One early study used kinetic theory to investigate the extent to which polarizable molecules attach themselves to slowly moving ions in a gas.[45] In this study two potentials were used. One was of the form $-kr^{-4}$ for $r \geq r_o$ and ∞ for $r \leq r_o$. This hard sphere potential was not found to be accurate and so a second potential of the form $k'r^{-12} - kr^{-4}$ was used and results in general agreement with experiment were obtained.

Another approach to the theory of ion clusters involved the use of statistical mechanics.[46,47] This study took into account the polarization force as well as chemical binding forces.

The Huckel molecular orbital approach and other

semi-empirical methods have been used in several studies. For example the Huckel method has been used to predict that the triangular geometry of H_3^+ is of lower energy than the linear geometry.[48-50] Semi-empirical theories and theories based on electrostatics have been used to predict possible structures for O_6^+ [35,51] and O_4^+, O_4^- and N_4^+.[52,53]

For the clusters H_n^+ a number of calculations have been done. Among the ideas which have been used to treat these clusters are the maximum symmetry model, the hydrogen bond model and the diatomics-in-molecules model.[48, 54, 55] The first model predicts that identical atoms in a polyatomic molecule or ion adopt the most symmetric geometry. For H_n^+ this suggests that the protons are equally spaced on the surface of a sphere - with possibly one proton at the center. This approach is not generally correct. The second model assumes that a proton acts to bind together two or more neutral fragments. It is assumed that the main attractive force arises from the ion-induced dipole interaction. This ignores the ion-quadrupole interaction as well as other forces in these systems and so is not even qualitatively correct (e.g., it predicts H_3^+ to be linear, when it is believed to be triangular). The third model assumes that the total energy of any polyatomic system is expressed in terms of the ground and excited state energies of all possible monatomic and diatomic fragments. This model predicts H_3^+ to be equilateral but gives wrong pre-

dictions for higher systems.

A general approach to ion-neutral bonding has been developed by Spears.[56] He uses repulsive potentials derived from semi-empirical calculations and a group of attractive potentials. These potentials include the ion-dipole (if a permanent dipole moment exists), ion-induced dipole, ion-quadrupole and other less important terms. For certain ions it is shown that the molecular hyperpolarizability is quite important. Using this approach excellent agreement with experiment is obtained in many cases.

A semi-classical model due to Poshusta, et al. is called the ion-bond model. This is similar to Spears' approach, but it is not made quantitative. It assumes that the binding in the ion clusters is primarily electrostatic. The interaction is between a central atomic ion and surrounding neutral fragments, which may be either molecules or atoms. This model predicts that in such clusters

(i) the binding energy is small

(ii) the bond lengths are large

(iii) the vibration frequencies of the neutral fragments are unchanged from their isolated values and

(iv) the electron densities are unchanged.

This model also predicts that in cluster ions containing more than one kind of atom, the most easily ionized atom plays the central role.

A number of ab initio calculations have been done on cluster ions. The system H_3^+ has been treated by a number of authors, since it is a simple two electron system, shaped like an equilateral triangle, with a side length of about 1.67 a.u. and a binding energy relative to H_2 and H^+ of about 5.0 eV.

Calculations on H_4^+ have also been done. Apparently this cluster ion has never been observed experimentally. A calculation was done on this sytem by Poshusta and Matsen[48] using the valence bond approach. Their basis set consisted of one s-type gaussian on each proton. With this limited basis set they predicted that H_4^+ is stable, belongs to the point group C_{3v} and has a binding energy relative to H_3^+ and H of 0.54 eV. Increasing the size of the basis set to two orbitals on each proton gave similar results. However, Schwartz and Schaad[64] repeated these calculations with five Gaussians on each proton and found no stable geometry. Poshusta et al.[57] confirmed this result. Later Huang, et al.[65] did more accurate valence bond calculations which also showed no stability for this ion. More recently, however, Poshusta and Zetik[66] did a VBCI study of this system and report that it is stable with a binding energy of 0.85 kcal/mole. They explain the absence of H_4^+ in mass spectrographic experiments to be due to the lack of a mechanism by which it might be formed.

It is interesting, in light of Poshusta's simple ion-

bond model, that a calculation has been done on H_4^{2+} and it has been predicted to be unstable.[68] This is in accord with the notion that the doubly positive charge will reside on two centers, since each center has the same ionization potential. These two positive centers will then repel each other with a Coulomb type force and the system will be unstable.

Poshusta and Matsen[48] did a VB calculation on H_5^+. Using a basis of one s-type Gaussian on each proton, they constructed a ten-term wave function. Their result was that H_5^+ is stable, has an elongated tetrahedral geometry (with symmetry D_2d) and a binding energy relative to H_3^+ and H_2 of 0.81 eV. They find the separation between nearest proton pairs is 1.5 a.u. - almost the same as H_2. Another calculation of theirs on this ion yielded similar results.[57]

A calculation of H_5^+ by Easterfield and Linnett,[25] in which they used the molecular orbital (MO) approach and the floating spherical Gaussian orbital (FSGTO) method of Frost,[69] yielded a geometry which differed from that of Poshusta. Their most stable geometry was one in which three protons are disposed in an isosceles triangle having one side length of 0.85Å and the other two of length 0.91Å. A line through the other two protons is at right angles to the plane of the triangle and the whole assembly has C_{2v} symmetry (a distorted tetrahedron). They feel that H_5^+ can then be regarded as an H_2 molecule polarized by the

neighboring H_3^+ triangle. They find a binding energy of 9 kcal/mole.

Huang, et al.[65] did both a VBCI and an MO-SCF calculation on H_5^+. Their VBCI calculations predicted extremely weak bonding. The MO-SCF calculation predicted a distorted tetrahedron with C_{2v} symmetry in which the H_2 sits about 3 a.u. from the H_3^+ apex and perpendicular to the plane of the H_3^+ triangle. This is similar to the geometry of Easterfield and Linnett. Their calculated binding energy is 4.25 kcal/mole. Since they regard H_5^+ as a loose molecular complex (of the form $H_3^+ \cdots H_2$) and because they believe that, in effect, it is composed of two closed shell systems which dissociate into closed shell systems, they feel that bonding in this system should produce very little extra correlation energy. For this reason, and because they used a large basis set, their results are felt to be reliable.

H_6^+ has been predicted to be unstable on the basis of a VB calculation.[48] It has been reported that calculations on H_7^+ have been carried out, but no details were given other than it had C_{2v} symmetry.[25]

A number of other calculations on cluster ions have been done. Poshusta et al.[57] have done calculations, using the VB method, on BeH_2^+, $LiHeH^+$, He_3^+, LiH_3^+, LiH_2^+, He_2H^+, HeH_3^+, and HeH_2^+, as well as those previously mentioned. These were all found to be stable. They also predicted that $He_2H_2^+$ HeH_4^+ are unstable.

Easterfield and Linnett[25] used the PSGTO method to predict that LiH_{2n}^{+}, n=1,2,3 are stable. They also suggest that BeH_{n}^{+}, with n odd, might be stable.

An interesting set of calculations were carried out on the systems $HeBe^{2+}$ and $NeBe^{2+}$.[27] These were LCAO-MO-SCF or Roothaan Hartree-Fock type calculations. Large basis sets of contracted Gaussians were used and both systems were predicted to be stable. $HeBe^{2+}$ was found to have a dissociation energy of 18.6 kcal/mole and $NeBe^{2+}$ had a dissociation energy of 13.2 kcal/mole. As previously discussed this calculation has implications for matrix isolation spectroscopy.

Computations have also been done on the energy surface of the ion HeH_{2}^{+}.[70,71] In the study done by Edmiston, et al. a CI calculation using pseudo natural orbitals was carried out and part of the energy surface was computed. They found that the correlation energy, which is about 25 kcal/mole, changes smoothly with internuclear separation and that the total change between reactants and products is only 3 kcal/mole. This suggested to Brown and Hayes that an LCAO-MO-SCF calculation might permit a study of the entire potential surface for this system. As a result of this they found a minimum corresponding to an He-H-H bond angle of 180°.

Ab initio calculations using the VBCI method have been done on $He_{2}H^{+}$ and it has been found to be a linear symmetric system with a dissociation energy of about 0.45 eV.[72]

Another system which has been carefully studied is BeH_2^+.[73] Both MO-SCF and VBCI calculations were carried out on this ion. It is predicted to be weakly bound in a $^2A_1$ state. The calculations indicate that this ion is triangular.

The molecule ion He_2^{2+} has been studied in some detail. Fraga and Ransil[74] did an SCF-MO-CI calculation on this system and found it to be metastable with a hump shaped potential curve.

It is possible to extend ab initio calculations on diatomic ions to small internuclear separations. In some cases these calculations can be related to the results of low energy scattering experiments involving the ion and atom making up the diatomic. In particular, if a repulsive potential can be derived from the scattering data this can be compared to a similar potential deduced from theoretical computations. For example, the system Li^+ - He was studied experimentally by Zehr and Berry.[79] They calculated the short range interaction (repulsive) potential for this system from low energy scattering data ($\lesssim$ 1000 eV). At these energies the Born-Oppenheimer approximation may be invoked.[113] They found that a Thomas-Fermi-Dirac (TFD) calculation of the repulsive potential at small internuclear separations have good agreement with experiment down to 0.3Å. Below this they found divergence between theory and experiment. Ab initio calculations had been made on Li^+He by Fischer,[76] Junker and Browne.[77] and Catlow, et al.,[78] and compared with the results of Zehr and Berry and also with

later experimental results on the same system by Aberth and Lorents.[80] Poor agreement was again found to exist below 0.3Å. More recent measurements of $Li^{\pm}$He collisions have shown the existence of inelastic and charge exchange channels and the energy variation with internuclear separation of the "summed" elastic, inelastic and charge transfer cross-sections is now in substantial agreement with published ab initio ground state calculations.[81-83]

More recently Giffen and Berry[75] have reported measurements of the elastic scattering of 100-800 eV Be ions by He atoms. They determined an effective interaction potential for internuclear separations $0.15 \leq R \leq 1.0$Å. Agreement of this potential with an interaction energy computed from a semi-classical TFD model was reported down to 0.3Å. Below 0.3Å there was serious disagreement between experiment and theory.

The preceding discussion has indicated that ab initio calculations have been usefully employed in predicting the energetics and geometries of a number of molecule ions and in fact, to date, this method has often been the only way geometries of these systems have been elucidated.

The ab initio methods most frequently employed are based on either the VB or MO approximations. Only the MO method will be discussed here.

The MO-SCF method in the LCAO approximation as developed by Roothaan and also called the Hartree-Fock-Roothaan method will be discussed in detail in Appendix 1.

Basically the problem is to find a set of molecular orbitals which can then be used to construct an antisymmetric wave function of the form

$$\Psi = a\chi \qquad (1$$

where a is an antisymmetrizing operator and

$$\chi = \phi_1 \phi_2 \cdots \phi_n \qquad (2$$

where ϕ_i is a one electron spin orbital.[86] The spatial part of this is first expanded as

$$x_i = \sum_k C_{ik}\, y_k \qquad (3$$

where the y_k are the atomic orbitals or basis functions. These basis functions are often centered on nuclei, but this is not always necessary.[69]

To find the coefficients it is necessary to solve an algebraic equation called the Roothaan equation. For closed shells this equation has the form [87]

$$\sum_{q=1}^{M} (F_{pq} - S_{pq}\epsilon_i) C_{iq} = 0 \quad i = 1, \ldots, n \qquad (4$$

where F_{pq} is an element of the Fock matrix and S_{pq} is an element of the overlap matrix. ϵ_i is an orbital energy and may be obtained by solving the secular equation[87]

$$|F_{pq} - S_{pq}\epsilon_i| = 0.$$

These equations in general have to be solved by an iterative procedure since F_{pq} depends on the C_q'S. In general if there are m basis functions there will be m eigenvalues and m orbitals. The extra m-n orbitals are called virtual orbitals

and are of use in constructing excited states for CI calculations.[84]

The open shell equations are somewhat more complicated and will be briefly discussed in Appendix 1.

Two basis sets in common use consist of Slater type orbitals (STO's) and Gaussian type orbitals (GTO's). Many others have been proposed.[88]

The GTO's have the form

$$e^{-\alpha r^2}$$

Usually they are multiplied by a function of the coordinates, in which case, if the function is a simple product of powers of coordinates, they are called cartesian Gaussians and have the form[88]

$$N x_A^l y_A^m z_A^n e^{-\alpha r^2} \qquad (5$$

where $x_A = x - A_x$, r_A = radial distance from A

l, m, n are zero or positive integers

and N is a normalization constant.

Gaussian functions are considerably easier to integrate in the type of three and four center integrals which appear in the Roothaan equation than are Slater functions. However, they are not as accurate at large distances from the nuclei, nor are they as accurate very close to the nuclei as are the Slater functions. In general, a Gaussian basis set must be two to five times larger than a Slater basis set to obtain the same accuracy. A discussion of Gaussian

basis sets has been given by Boys.[96] For many of the systems to be discussed here the Hartree-Fock-Roothaan method is especially well suited. In particular, for closed shell systems which dissociate into closed shell systems, the interaction energy should go to the proper value in the limit of large internuclear separations.[90] Even in some open shell systems the calculated energy goes to the right limit as R goes to infinity. In general this is not always true of MO calculations, which frequently yield the wrong limiting value to the energy of the separated system. Examples of this can be found in reference 91.

A number of general programs exist for carrying out MO calculations on molecules or atoms. The set of programs used here for all calculations to be reported is called POLYATOM.[92-94] This implements the method of Roothaan with Gaussian basis sets. A brief description of POLYATOM will be given in Appendix 2.

II

THE CLUSTER IONS H_n^+

A series of calculations were carried out on the cluster ions H_n^+ using the LCAO-MO-SCF method. This work will emphasize calculations on the system H_{11}^+. The other calculations were done by Dr. S.W. Harrison.

The basis set used in all these calculation- consisted of four s-type Gaussians on each proton, which were contracted into two functions. One was a set of three Gaussians and the other was one primitive Gaussian. The exponents and contraction coefficients were obtained from reference 111 and are recorded in Table 5. Calculations by Dr. Harrison indicated that this basis set predicted a reliable geometry when used in a calculation on H_5^+ as compared to previously published results using more extensive basis sets.[65]

Certain assumptions were made in order to make these calculations tractable. The first one, already mentioned, was the use of a small basis set. The second assumption, based on the fact that these clusters are weakly bound and assumed to be of the form $H_3^+ \cdots (H_2)_n$, was that the H_3^+ triangle was the central ion in each of these systems. In fact, for all clusters higher than H_5^+ it was assumed that

H_3^+ is an equilateral triangle with a side length of 1.66 a.u.[63] The H-H distance in all H_2 pairs was held at 1.40 a.u.The third assumption was that all bonds which could be interchanged by symmetry operations of the point group to which the cluster was assumed to belong in a given calculation were varied simultaneously.

H_3^+, as already mentioned, is an equilateral triangle. Calculations on the electron distribution in this system[95] indicate that the negative electronic charge is primarily in the center of the H_3^+ triangle and that the protons are relatively "bare" and positive.

H_5^+ may also be written $H_3^+ \cdot (H_2)$. The H_2 molecule is arranged so that its axis is orthogonal to the plane of the H_3^+ triangle and its center is 3.0 a.u. off the tip of the H_3^+ triangle. This may be explained by invoking an argument similar to the general argument used by Spears,[56] in which the primary bonding forces in cluster ions are assumed to be electrostatic. The two strongest of these forces, in cluster ions with nonpolar neutrals, are the ion-induced dipole force and the ion-quadrupole moment force. The ion-induced dipole potential has the form[97]

$$V(e) = \frac{-\alpha Q^2}{2R^4} \qquad (6$$

where Q is the charge on the ion, is the polarizability of the neutral and R is the ion-neutral distance. The second force arises from the ion-quadrupole moment interaction and has the form[56]

$$V(R) = \frac{QM}{2R^3}(3\cos^2\Theta - 1) \qquad (7$$

where Q is the charge on the ion, M is the quadrupole moment of the linear neutral molecule and R is the distance (ion to center of mass). Θ is the angle between the molecular axis and the vector R.

Since the polarizability of H_2 is greater along its axis than perpendicular to it[97] the ion-induced dipole interaction favors the orientation with the axis of the H_2 molecule in the plane of the H_3^+ triangle and pointing along the line passing through both the apex of the triangle and its center. It should be pointed out that this assumes the proton at the apex of the H_3^+ triangle is essentially bare of electrons and thus acts like a positive charge. That this geometry is not correct may be explained by noting that the quadrupole moment of H_2 is positive.[114] From the potential energy given in equation 7, it is seen that this interaction favors the perpendicular orientation. This does not eliminate the possibility that the H_2 molecule will lie in the plane of the H_3^+ triangle but perpendicular to the line through the center and the apex of the H_3^+ nucleus. However, it can be argued that the in-plane configuration would be energetically less stable than the out-of-plane orientation because of the repulsions between the two protons and the H_2 molecule and the two protons in the H_3^+ behind the apex. It should be noted in this regard that ab initio calculations

have indicated that the in-plane orientation is less stable than the out-of-plane orientation.[48]

The binding energy of H_5^+ relative to dissociation into H_3^+ and H_2 was found to be 6.0 kcal/mole with this basis set. With a more accurate basis set, including p function, the binding energy was found to be 4.25 kcal/mole. This agreed with the result obtained by Huang, et al.[65]

A reasonable way of constructing H_7^+ would be to add an H_2 molecule at the second apex of the H_3^+ triangle,[65,25,98] so that this system would have C_{2v} symmetry. This H_2 would also be arranged orthogonally to the plane of the H_3^+ triangle. This indeed was found to be the best geometry for this molecule. The length from the center of either H_2 pair to the center of the H_3^+ triangle at the equilibrium distance was found to be 4.4 a.u. and the dissociation energy relative to H_5^+ and H_2 was found to be 0.4 kcal/mole.

For H_9^+ it seemed reasonable to assume that the third H_2 pair would be located off the tip of the H_3^+ triangle and arranged orthogonally to the plane of the triangle. The distance from the center of any H_2 pair to the center of the H_3^+ triangle was found to be 4.5 a.u. and the bond energy relative to H_7^+ and H_2 was 2.5 kcal/mole. The symmetry of this system was D_{3h}.

The ion H_{11}^+ which will be discussed in more detail

later, was found to have the additional H_2 pair with its axis along the principal axis of symmetry of H_9^+. The over-all symmetry was C_{3v}. This geometry maximizes the interaction between the quadrupole moment of the added hydrogen molecule and the net negative charge at the center of the H_3^+ nucleus. The distance from the center of the H_3^+ to the center of the H_2 pair was estimated to be 5.8 a.u., while the distance from the center of any of the other three H_2 pairs to the center of the triangle is estimated to be 4.5 a.u. The binding energy was estimated to be 0.6 kcal/mole relative to H_9^+ and H_2.

In H_{13}^+ the fifth H_2 molecule is added onto the principal axis of symmetry of H_{11}^+, opposite to the fourth H_2 pair. The distance from the center of this H_2 pair to the center of the H_3^+ triangle is 6.0 a.u. and the binding energy is 0.6 kcal/mole. The over-all symmetry is D_{3h}.

A fairly extensive search was carried out to determine the best geometry of H_{15}^+.It was originally suggested that this is stable when arranged as six hydrogen molecules packed in an octahedron around an H_3^+ nucleating center.[7] This was not found to be the case. Instead, the most stable structure was obtained by adding to the H_{13}^+ structure an H_2molecule with its center in the σ_h plane of symmetry of H_{13}^+. The distance from the center of this H_2 pair to the center of the H_3^+ triangle is 7.5 a.u. and the binding energy of this molecule is 0.3 kcal/mole relative

to H_{13}^+ and H_2. The symmetry is C_{2v}.

It is interesting that the above calculations show that each H_n^+ cluster ion can be formed by the addition of one H_2 pair to the basic structure of the previous member of the series. It should also be kept in mind, when comparing these results to experiment, that the actual machanism by which H_n^+ clusters form will depend on the conditions of a particular experiment.[104] The total energies, bond energies and geometries of these cluster ions are listed in Tables 1 and 2 and Figure 1. All of the above results have been reported elsewhere.[99] The arguments given here pertaining to electrostatic forces governing the geometries of these systems are only qualitative and cannot be made quantitative without a detailed treatment of the repulsive forces in these systems.

Calculations on the H_{11}^+ cluster ion will now be described. Two geometries were tried. The first is a tetrahedral arrangement since it was originally thought this would be favored.

A program was written to compute the coordinates of the H atoms. The symmetry appropriate to this geometry (C_{3v}) was used as a basis for calculating the coordinates. Also as a further guide three dimensional models of this and other H_n^+ cluster ions were constructed. These were helpful in visualizing the structures of the clusters. The energy cut-off used in this and all other calculations which follow was 5×10^{-5} a.u.

The first geometry tried had C_{3v} symmetry, with the H_3^+ bond distance set at 1.66 a.u. The H_2 bond length was set at 1.4 a.u. This was a tetrahedral arrangement, with the axes of the three H_2 pairs, below the plane of the H_3^+ triangle, perpendicular to the radii from the center of the triangle. This accords with the qualitative argument based on the ion-quadrupole interaction. The fourth H_2 pair was placed above the plane of the H_3^+ triangle and its axis lay along the principal axis of symmetry of the cluster. Two coordinates were varied. One was the distance from the center of any H_2 pair, below the H_3^+ plane, to the center of the H_3^+ triangle. The other was from the center of the H_5^+ triangle to the center of the H_2 pair with its axis along the principal axis of symmetry.

When both these coordinates were varied simultaneously a minimum was found at 4.8 a.u. This may be seen in Figure 2 and Table 3. This minimum was found to be above the sum of the energies of H_9^+ and H_2. Thus it appears this geometry is not stable. When the first coordinate was held at 4.8 a.u. and the second varied no minimum was found and the energy was always above that of H_9^+ and H_2. This is summarized in Table 3. Finally the H_2 molecule along the principal axis of symmetry was tilted perpendicular to this axis, but without significant improvement in energy.

The second geometry which was tried had the centers of the three H_2 pairs in the plane of the H_3^+ triangle and the fourth H_2 pair with its axis along the principal axis of

of symmetry of H_9^+. This geometry is depicted in Figure 1. The same two coordinates were varied here as in the preceding case. These results are recorded in Table 4. Figure 3 shows the results obtained when these two coordinates were varied simultaneously. From this data the binding energy and equilibrium geometry were estimated. It is seen from Table 2 that H_{11}^+ is only slightly stable relative to H_9^+ and H_2. In Table 5 the exponents and contraction coefficients for these calculations are listed. In Table 6 the MO coefficients are listed for the stable geometry of H_{11}^+ close to equilibrium.

A third geometry was considered. This was a tetrahedral arrangement with the axes of the H_2 pairs along radii from the centers of the tetrahedron to the corners. This was rejected because the interaction between the quadrupole of the H_2 pairs and the ion would not give rise to a strong attractive force.

III

CLUSTERING OF HELIUM ON BERYLLIUM IONS

Hayes and Gole have calculated the $Be^{2+}He$ interaction energy using the MO-SCF method.[27] They carried out their calculations because of the possible significance they may have for matrix isolation spectroscopy. They predicted that $Be^{2+}He$ is stable and has a binding energy of 18.6 kcal/mole. In their calculation a basis set of thirteen grouped Gaussians was used, constructed from 18 primitive Gaussian orbitals.

Because of the possibility that Be^{+} and Be^{2+} ions might serve as central ions in clusters when the neutrals are rare gas atoms, calculations have been performed by us on the systems $Be^{2+}He$, $Be^{2+}He_2$, and $Be^{+}He$. These are ab initio calculations of the Hartree-Fock-Roothaan type. Except for $Be^{+}He$, these are closed shell systems which dissociate into closed shell fragments. $Be^{2+}He$ has a $^1\Sigma^+$ ground state arising from the $1\sigma^2 2\sigma^2$ orbital configuration. $Be^{2+}He_2$ has a $^1\Sigma_g^+$ ground state arising from a $1\sigma_g^2 2\sigma_g^2 3\sigma_u^2$ orbital configuration. Since Be^{2+} and He lie below Be^{+} and He^{+} in energy,[105] $Be^{2+}He$ dissociates into Be^{2+} and He and Be^{2+} and He and $Be^{2+}He_2$ dissociates into $Be^{2+}He$ and He. $Be^{+}He$ is an open shell system having the orbital configur-

ation $1\sigma^2 2\sigma^2 3\sigma$. This gives rise to a $^2\Sigma^+$ state. Even in this case where dissociation is of the form

$$Be^+He \longrightarrow Be^+ + He \qquad (8$$

the MO method can yield reliable results. In fact, for all these systems the energy surfaces produced are expected to be quite parallel to the experimental surfaces, even for configurations that are far from equilibrium values. This results from the fact that the ion-induced dipole interaction, which is believed to be the chief attractive force in these systems, is fairly weak and is not expected to produce extra correlation energy effects not accounted for in the Hartree-Fock-Roothaan method.

The Gaussian basis sets used here were derived from several sources. For $Be^{2+}He$ the basis set consisted of 23 Gaussians. These included ten s- and six pz-orbitals on Be and five s- and two pz-orbitals on He. The exponents were obtained from Huzinaga[100] and Kaufman and Sachs.[101]. These are listed in Table 7 and the calculated energies at various internuclear distances are reported in Table 8 and Figure 4. The bond energy was computed by taking the difference between the energies of the molecule and the separated atom and ion. The energies of the atom (He) and ion (Be^{2+}) were calculated with the same program and basis sets as were used in the molecular calculation. However, only s-type orbitals participated in the ground state atom and ion wave functions, as expected. The bond energy is found to be 18.6 kcal/mole and the bond length was estimated

to be 2.71 (±.01) a.u. An examination of the coefficients near the equilibrium internuclear distance (Table 10) indicates that the double positive charge is localized almost entirely on the Be^{2+} ion with the electron distribution of the helium atom slightly polarized towards this positive charge, as expected for an ion-induced dipole bond.

The closed shell system $Be^{2+}He_2$ was treated by a similar method to that used above. A basis of thirty primitive Gaussians was used. This consisted of five s-type orbitals and two pz-type orbitals on each helium atom and ten s- and six pz-type orbitals on the beryllium ion. The exponents were taken from the same sources as above.[100,101] The exponents are listed in Table 11.

Only the linear case was investigated. Any non-linear geometry is expected to increase the repulsion between helium atoms with no other compensatory advantage and hence would not be favored. It was assumed, of course, that the two helium atoms were on opposite sides of the beryllium ion. This accords with the notion that the central ion in a cluster has the lowest ionization potential (see Introduction).

In Table 12 are listed the energies calculated at various internuclear separations. Figure 5 depicts the variation of energy with the simultaneous variation of the two ion-atom distances. The MO coefficients are given for a configuration near the potential minimum in

Table 13. Again it is seen that the MO coefficients imply an ion-induced dipole bond. Finally Table 9 lists the dissociation energy for the reaction

$$Be^{2+} (He)_2 \longrightarrow Be^{2+}He + He \qquad (9$$

which is 17.7 kcal/mole, with an internuclear distance of 2.72 ($\pm$0.01) a.u. This is in reasonable accord with the fact that the double positive charge in $Be^{2+}He$ is localized on the Be^{2+} ion, so that it presents a similar interaction to a second helium atom approaching from the non-bonded side as it did to the first He atom. One might extrapolate to conclude that clusters $Be^{2+}He_n$ for $n > 2$ may also be stable. However, in such clusters some of the helium atoms will be closer to each other than they are in the linear case. The resulting increased repulsion will decrease the stability of such clusters. The magnitude of this increased repulsion can be estimated from empirical relations for the repulsion between helium atoms[102] and it appears such clusters will be stable.

The molecule ion $Be^{+}He$ has also been studied. As stated previously, it is believed to have a ground state arising from the $1\sigma^2 2\sigma^2 3\sigma$ orbital configuration. The possibility that a $^2\Pi$ state, arising from the orbital configuration $1\sigma^2 2\sigma^2 1\pi$, might be the true ground state seems unlikely since the 3σ orbital would be expected to lie below the 1π orbital at all internuclear distances.[103] The Roothaan double operator open shell

procedure was used to calculate the energy of this system.[85] Only the $^2\Sigma^+$ state energy was calculated. The parameters α, β and γ as required in the POLYATOM open shell program PA42 were taken from Roothaan's paper[85] and were

$$\alpha = 0,\ \beta = -2.0 \quad \text{and} \quad \gamma = 0.5$$

The results of this calculation are listed in Table 14. It is seen that the mimimum energy occurs at about 6.4 a.u. ($\pm$0.1) and the binding energy is about 0.12 kcal/mole (see Table 9). This was calculated by subtracting the sum of the atom (He) and ion (Be+) energies from the energy of the molecule at its equilibrium internuclear distance. The atom and ion energies were calculated with the same basis set used to calculate the molecular energy. Twenty-three basis functions were used with ten s- and six pπ-orbitals on Be and five s- and two pπ-orbitals on He. The exponents were taken from the literature[100,101] and are listed in Table 15. The MO coefficients near the equilibrium internuclear distance are listed in Tables 16 and 17. They show an ion-induced dipole bond.

As before the energy cut-off in all these calculations was 5×10^{-5} a.u. This corresponds to about 0.03 kcal/mole and so the bond energy might be off by as much as 0.09 kcal/mole. This however is an extreme upper limit to the error, so that the system is almost certainly stable. The calculated value of the bond energy might, however, be in error by a large relative amount.

To explain the long bond length and extremely weak bonding in this system it should be noted that, from the attractive potential listed in eq.5, reducing the charge on the Be from +2 to +1 reduces the attractive force by one-quarter. The repulsive force may also be larger. The additional electron in $Be^{+}He$ is localized primarily on the Be atom (as may be seen from the MO coefficients- see Table 16) and is not strongly involved in bonding. It does seem, however , that the charge density associated with this electron is axially symmetric and pointing towards the He atom. Thus it apparently serves only to increase the repulsion in this system.

Some of the results described above are reported elsewhere.[107]

IV

CLUSTERS OF HELIUM AND CARBON IONS

It is well known that helium atoms and carbon ions exist in interstellar space. It is believed that a charge transfer process of the form

$$C^{2+} + He \longrightarrow C^{+} + He^{+} \qquad (10$$

occurs in the interstellar medium. Attempts have been made to calculate rate coefficients for the above process.[106]

The possibility that helium atoms might cluster on carbon ions has been investigated. In particular, the ions HeC^{2+} and HeC^{+} have been studied theoretically by us. Clustering of helium atoms on carbon ions would be in accord with Poshusta's Ion-Bond model[57] (see also Introduction). Since this model predicts that in any cluster the most easily ionized atom plays the central role, both C^{2+} and C^{+} ions would be suitable as central ions around which He atoms could cluster (see reference 105). Presumably in such systems the bonding would be of the ion-induced dipole type. Since this interaction leads to weak bonds, systems of this type tend to have smaller dissociation energies, smaller vibrational frequencies and longer bond

lengths than other similar but covalently bonded molecules.

The molecule ion HeC^{2+} is a closed shell system with orbital configuration $1\sigma^2 2\sigma^2 3\sigma^2$. The ground state is thus $^1\Sigma^+$. HeC^+ is more complicated. It is an open shell system whose ground state might be $^2\Pi$ arising from the $1\sigma^2 2\sigma^2 3\sigma^2 1\pi$ configuraton or it might be a $^2\Sigma^+$ state arising from the $1\sigma^2 2\sigma^2 3\sigma^2 4\sigma$ configuration. The diatomic CH, which is isoelectronic with HeC^+ is known to have a $^2\Pi$ ground state.[108] This however does not rule out the possibility that He C^+ has a $^2\Sigma^+$ ground state. The molecule may have a much longer bond length than CH, which would tend to favor a $^2\Sigma^+$ ground state, as may be seen from a molecular orbital correlation diagram.[103] For reasons to be discussed later, only the $^2\Pi$ state of HeC^+ was considered here.

Since experimentally it is known that the sum of the energies, assumed negative, of He and C^{2+} lies below the sum of the energies of He^+ and C^+ and that the sum of the energies of He and C^+ lies below He^+ and C,[105] dissociation of the molecule ions is expected to take place as follows:

$$HeC^{2+} \longrightarrow He + C^{2+}$$
$$HeC^{+} \longrightarrow He + C^{+} \qquad (11$$

The calculations were done using Gaussian basis sets. For HeC^{2+} a basis set of thirty Gaussians was em-

ployed. These include ten s- and six pπ-type orbitals on the carbon and nine s- and five pπ-type orbitals on helium. The separated atom and ion energies were calculated with the same basis set used for the molecules. In Table 18 the exponents of the basis functions are exhibited. These were obtained from the literature.[100,101,109] In Table 19 are listed the energies as a function of internuclear separation, including the sum of the calculated atom and ion energies at infinite separation.

In the case of He C^+ it was assumed that this system has a $^2\Pi$ ground state. Computations on this system were done using Roothaan's double operator formalism.[85] The basis set consisted of thirty-five Gaussian functions, including five s-, two pπ-, two px-, and two py-orbitals on helium and nine s-, five pπ-, five px-, and five py-orbitals on carbon with exponents taken from the literature.[100,101,109] In Table 20 these exponents are exhibited. The separated atom and ion energies were again computed with the same basis sets. The calculated energies for HeC^+ are listed in Table 19. The constants α, β, γ called for in the POLYATOM open shell SCF program were chosen to be

$$1.3333333, \quad 1.33333333, \quad 0.25.$$

Attempts to calculate the $^2\Sigma^+$ state of HeC^+ failed due to a lack of convergence of the iterative process used. As many as fifty iterations were used in this calculation, and, despite the use of special averaging

and extrapolation subroutines, no convergence of the SCF energy occurred. In this calculation the internuclear separation was held at 3.3 a.u.

The spectroscopic constants were obtained by doing a least squares fit of the calculated energies to a Hulbert-Hirschfelder function.[110] The actual fitting of the data was carried out by Dr. G. A. Henderson. The calculated spectroscopic constants are listed in Table 21.

The results indicate that both molecule ions are weakly bound. HeC^{2+} has an estimated dissociation energy of 9.3 kcal/mole and a fairly low vibrational frequency (493 cm^{-1}) for a first row diatomic.[108] This is consistent with the weak ion-induced dipole interaction believed to dominate the bonding in this system. It should be noted that experience with calculations of this type indicate that bond lengths can be predicted to within 3% and vibrational frequencies are accurate to within 10-20%.[91, 87]

The $^2\Pi$ state of HeC^+ is extremely shallow. The binding energy can only be estimated to be $\geq$ 0.55 kcal/mole. Due to this, the dissociation energy and spectroscopic constants are probably less accurate than for HeC^{2+}.

In Figure 6 the potential energy surfaces for these systems are exhibited. In Tables 22, 23, and 24 the MO coefficients near the equilibrium internuclear separations are listed for these ions.

The results discussed here have been reported elsewhere.[112]

V

SOME UNSTABLE IONS

The ion He_2^{2+} is believed to be metastable.[74] This means that while its potential curve shows a minimum, it also has a maximum and the energy of the dissociated products is lower than the energy of He_2^{2+} at its potential minimum.

It was thought worthwhile to study the closed shell system He_3^{2+} to see if a stable geometry could be found. Only the linear case was treated. The calculations were done with Gaussian basis sets and the orbital exponents used are listed in Table 25.

No stable linear geometry of He_3^{2+} was found relative to dissociation into 2He and He^{2+}. The energy of 2He and He^{2+} is known experimentally to lie above $He_2^+ + He^+$, which are the presumed dissociation products. Thus, He_3^{2+} is probably unstable. It appears therefore that a doubly charged helium nucleus may not act as a nucleating center for a helium cluster. The calculated energies are listed in Table 26.

It has also not been possible to find any stable geometry for the closed shell system $He^{2+}\ (H_2)_2$.

VI

$He\text{-}Be^{2+}$ INTERACTION ENERGY AT SMALL INTERNUCLEAR DISTANCES

An interesting problem is that of the low energy scattering of Be^{2+} ions by He atoms. This has been investigated experimentally by Giffen and Berry.[75] A theoretical treatment of this problem, using the LCAO-MO-SCF method to compute the interaction energy at small internuclear distances is possible for the following reasons:

i) The system has only four electrons, so an ab initio treatment is possible.

ii) The $1\sigma^2 2\sigma^2$ ground state of $He\text{-}Be^{2+}$ goes over directly to the $1s^2\ 2s^2$ united atom ground state of C^{2+}, so the calculations will be accurate at short distances.

iii) The interaction energy goes to the proper limit as $R \to \infty$, since the $He\text{-}Be^{2+}$ ion and the separated atom (He) and ion (Be^{2+}) are closed shell systems.[90]

iv) The Born-Oppenheimer approximation should be valid for ion energies used in the experiment (100-800 eV).[113]

To find the interaction energy of the He atom and the

Be ion at a given internuclear separation, the total energy of the atom ion system is computed with basis sets of atomic orbitals on each center that are flexible enough to allow for the distortion of charge on each center at small separations. The separate basis sets are also used to calculate the energies of the free atom and the free ion. Since both the He atom and the Be^{2+} ion have filled s-orbitals, the p-type basis functions included in the atom-ion system need not be used. The interaction energy is then the total energy of the atom ion system minus the sum of the free atom and the free ion energies. The limit of the electronic energy of the $HeBe^{2+}$ system as the internuclear distanct $R \rightarrow 0$ is found by computing the energy of the united atom C^{2+} with the same basis set, again only using spherically symmetric atomic orbitals.

The actual computations were carried out using the LCAO-MO-SCF method. The method is that of Roothaan with Gaussian basis sets employed. The basis set consisted of ten s- and six p_z-type functions on the Be ion and nine s- and five p_z-type functions on the He. The orbital exponents were taken from the literature[100,101,109] and are listed in Table 27. The results of these computations are listed in Table 28 and were least squares fitted to a Born-Mayer type potential. The result, with the interaction energy in electron volts, is:

$$V(R) = 944 \exp(-6.23R) \qquad (12$$

for the range $0.16 \leq R \leq 0.794$Å. When compared to the calculated values this expression gives an interaction energy which is lower by about 10% at 0.16Å and about 4% at 0.79Å, and is higher by about 6% at 0.32Å. The interaction energy derived from scattering data by Giffen and Berry[75] has been reported to have the form

$$V(R) = 600 \exp(-5.70R) \qquad (13$$

for $0.15 \leq R \leq 1.0$Å.

The results of the LCAO-MO-SCF calculation, and the values obtained from the two Born-Mayer potentials for the same value of R are shown in Table 29. The two Born-Mayer potentials are also plotted in Figure 7. They differ by only 0.213 eV at 0.79A, but there is a spread of 108 eV as R decreases to 0.16A.

Table 30 gives the ground state energies obtained from the free atom (He) and free ion (Be) and for the united atom C^{2+} system. For comparison the experimental values and the best reported SCF values obtained by Roothaan et al.[114] are also shown. Inspection of the Table shows that the basis sets used here give energies that compare favorably with the best reported values. Comparison with the experimental values shows that the correlation energy for helium is about 1.1 eV while that for Be^{2+} is about 1.2 eV. The correlation energy for the ground state of C^{2+} is about 3.8 eV. The interaction energy is the difference between the total energy and that of the separated atom and ion. The error in the

interaction energy for the molecule can be estimated in a first approximation by subtracting the correlation energy of the separated systems from that of the united atom, giving a magnitude of 1.5 eV. This method implies a monotonic increase in correlation energy ongoing from the separated atom to the united atom and this may give a value which is too low. However, the correlation energy is not expected to be a very sensitive function of the internuclear distance and therefore the maximum correlation error in the molecule is not expected to be far different than the value for the united atom. Hence we expect the estimate (1.5 eV) of the error in the interaction energy to be of the correct order of magnitude.

It seems reasonable, therefore, that in the case of $HeBe^{2+}$, the total error in the interaction energy, due to electron correlation, would be of the order of ten eV. Since the difference between the single determinant SCF calculation and the experimental results below 0.3Å internuclear separation is as much as another order of magnitude larger, correlation energy alone cannot explain the lack of agreement.

The total electronic energy, plotted as a function of internuclear separation, goes smoothly to the united atom ground state value (-36.4070 a.u.), as shown in Figure 8. The energy of the lowest occupied orbital, which corresponds to the ($1s^2$) orbital for the separated Be^{2+} ion,also goes

smoothly to the $1s^2$ orbital energy for C^{2+}. The variation of the other orbital with energy is not monotonic, but exhibits a small maximum at about R = 0.3 a.u. and falls to the $2s^2$ orbital value for C^{2+} which it was approaching from below for larger separations. It was felt that perhaps the basis sets did not allow for enough distortion of the charge distribution at some values of R so slightly larger sets of p functions were used on both the He and Be^{2+} centers. This did not eliminate the maximum which is 0.2 a.u. above the $2s^2$ orbital energy of C^{2+}. The orbital energies are listed in Table 31. Table 32 lists the exponents of the expanded basis set. The maximum in orbital energy may be indicative of configuration mixing at R = 0.3 a.u. The work of Miller and Present[115] for He_2 is suggestive of this, but further calculations are necessary in the case of $HeBe^{2+}$ to assess the importance of such mixing, particularly since orbital energies may be sensitive to the orbital exponents.[116]

The lack of agreement between theory and experiment may be explained as being due to inelastic excitations of the He atom and charge exchange between atom and ion, both of which reduce the flux in the elastic channel. As Giffen and Berry[75] point out, elastic scattering resulting in charge exchange was not observable with the method of measurement used in their experiments.

Further study of excited state potential curves and possible curve crossing effects are indicated.

VII

SUGGESTIONS FOR FURTHER WORK

There are many possibilities for further work in this field. Calculations on the H_n^+ cluster ions may be extended by using p functions. These would introduce a more accurate representation of polarization into the calculations. Also semi-empirical calculations might be done on higher members of this series.

The $^2\pi$ state of the molecule ion $HeBe^+$ might be calculated in order to determine with certainty whether it lies below the $^2\Sigma^+$ state. Also further attempts could be made to calculate the $^2\Sigma^+$ state of HeC^+.

The system He_4^+ is an interesting ion whose structure is unknown. It has been detected experimentally and might be worthwhile treating theoretically. Further calculations on the scattering of Be^{2+} ions by He atoms are warranted. These could include C.I. studies and studies of excited states, which might throw light on the precise nature of the scattering process. Also the scattering of C^{2+} ions by He might be studied theoretically, by methods similar to those used in the $HeBe^{2+}$ case.

A variety of open shell systems of the cluster ion type are possible and might be studied. For example, B^+He and N^+He might be stable systems.

Appendix I

The Hartree-Fock-Roothaan approach to SCF theory has been discussed in a number of published works.[84-87,90,91, 118, 119] A short outline of this theory will be given here.

The MO-SCF method is based on the variation theorem. This states that if the energy is evaluated from an approximate wavefunction, which meets certain conditions (e.g., boundary conditions), then that energy will be an upper bound to the lowest energy eigenvalue of the Hamiltonian,[119] that is

$$\frac{\langle \Psi | \mathcal{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle} \geq E_o \qquad (14$$

It should be noted that if Ψ_n is an approximate wavefunction of different spin or symmetry from the ground state wavefunction, then

$$\frac{\langle \Psi_n | \mathcal{H} | \Psi_n \rangle}{\langle \Psi_n | \Psi_n \rangle} \geq E_n \qquad (15$$

where E_n is the lowest eigenvalue of the Hamiltonian associated with the lowest state of the same symmetry as Ψ_n.

In the orbital approximation, each atomic or molecular wavefunction is assumed to be representable as a product of orbitals. In order to satisfy the Pauli principle this product is antisymmetrized. This may be accomplished by writing the wavefunction as a Slater determinant. This has the form[87]

$$\Psi = |\psi_1(1)\bar{\psi}_1(2)\ldots\psi_n(2n-1)\bar{\psi}_n(2n)| \quad (16$$

where ψ_i is an orbital and $\bar{\psi}_i$ is the orbital with opposite spin. We are assuming here that the wavefunction describes a closed shell. The term closed shell as used here refers to a set of orbitals such that

i) Every orbital occurs twice, namely, once with either spin and

ii) If there is degeneracy on account of symmetry, the orbitals which are degenerate form a complete degenerate set.

The Hamiltonian for the system is taken to have the form[87, 118]

$$\mathcal{H} = \sum_i H(i) + \sum\sum_{i<j} \frac{1}{r_{ij}} \quad (17$$

where

$$H(i) = -\frac{1}{2}\nabla_i^2 - \sum_a \frac{Z_a}{R_{ia}} \quad (18$$

and r_{ij} is the distance between electrons, R_{ia} is the distance between electron i and nucleus a and Z_a is the charge on nucleus a. Atomic units are used throughout, and, in the Born-Oppenheimer approximation, the nuclear-nuclear repulsion term is a constant. For this reason this term is omitted from the Hamiltonian for calculational purposes.

It is assumed that all molecular orbitals are orthonormal (i.e., $\langle\psi_i|\psi_j\rangle = \delta_{ij}$). Then the total energy may be written[87]

$$E = 2\sum_i H_i + \sum\sum_{ij}(2J_{ij} - K_{ij}) \quad (19$$

where

$$H_i = \langle \psi_i(1) | H(1) | \psi_i(1) \rangle$$

$$J_{ij} = \langle \psi_i(1)\psi_j(2) | \frac{1}{r_{ij}} | \psi_i(1)\psi_j(2) \rangle$$

$$K_{ij} = \langle \psi_i(1)\psi_j(2) | \frac{1}{r_{12}} | \psi_j(1)\psi_i(2) \rangle$$

The condition is then imposed on the energy E that for any variation in the orbitals, E = 0. This, together with the condition $\delta\langle\psi_i|\psi_j\rangle = 0$ insures that the energy is a minimum. In order that these two conditions be satisfied, the method of Lagrangian multipliers is used.[84] The variational equation is then

$$\delta E - 2\sum_i\sum_j \epsilon_{ji}\left(\langle\delta\psi_i|\psi_j\rangle + \langle\psi_i|\delta\psi_j\rangle\right) = 0 \quad (20$$

Ultimately this leads to an equation of the form

$$F\psi_i = \sum_j \epsilon_{ji}\psi_j \quad (21$$

where

$$F = H(1) + \sum_j (2J_j - K_j) \quad (22$$

H(1) has been defined previously (eq.18) and

$$J_j(1)\psi_i(1) = \langle \psi_j(2)|\frac{1}{r_{12}}|\psi_j(2)\rangle\psi_i(1) \quad (23$$

$$K_j(1)\psi_i(1) = \langle \psi_j(2)|\frac{1}{r_{12}}|\psi_i(2)\rangle\psi_j(1)$$

It can be shown that ϵ_{ji} are the elements of an Hermitian matrix,[87] so that

$$\epsilon_{ij} = \epsilon^{*}_{ji} \text{ for all } i, j$$

It is possible to diagonalize this matrix to obtain

$$F\psi_i = \epsilon_i \psi_i \qquad (24$$

which is a pseudo-eigenvalue equation.

The solutions of these equations form a set of orbitals called cannonical orbitals. The following facts are true of them and of the orbital energies.

i) All eigenvalues are real

ii) All eigenfunctions (orbitals) are, or can be chosen to be, orthogonal.

iii) The orbitals may be grouped in sets such that each set belongs to an irreducible representation of the symmetry group of the molecule.

iv) The orbitals can always be chosen real.

It is of interest that the total energy can be written in the form

$$E = \sum_i \left(H_i + \epsilon_i \right) \qquad (25$$

and that the orbital energy can be written

$$E_i = Hi + \sum_j (2J_{ij} - K_{ij})$$

The Hartree-Fock equations are difficult to solve for molecules. The LCAO method is preferable, though less accurate. In this approximation each orbital is expanded

into a linear combination of atomic orbitals or basis functions. This expansion has the form[87]

$$\Psi_i = \Sigma_\rho C_{i\rho} \phi_\rho \qquad (26$$

where the ϕ_p are the basis functions. As discussed previously (see Introduction) two popular sets of basis functions are the Slater type orbitals (STO's) and the Gaussian type orbitals (GTO's). The Hartree-Fock equations now take the form

$$\Sigma_q (F_{pq} - S_{pq} \epsilon_i) C_{iq} = 0 \quad i = 1, \ldots, n \qquad (27$$

where $S_{pq} = \langle \phi_p / \phi_q \rangle$ (28

$$F_{pq} = \langle \phi_p / F / \phi_q \rangle$$

F_{pq} is called an element of the Fock matrix and S_{pq} is an element of the overlap matrix. This is an algebraic equation which must be solved by an iterative procedure since F depends on the coefficients as[120]

$$F_{pq} = H_{pq} + \Sigma_{\lambda\sigma} P_{\lambda\sigma} [(pq/\lambda\sigma) - \tfrac{1}{2}(p\lambda/q\sigma)] \qquad (29$$

where $(pq/\lambda\sigma) = \langle \phi_p(1) \phi_q(1) / \frac{1}{r_{12}} / \phi_\lambda(2) \phi_\sigma(2) \rangle$ (30

and $P_{\lambda\sigma} = 2 \Sigma_i C^*_{\lambda i} C_{\sigma i}$

In general there will be an extra set of orbitals among the solutions which are not filled and are called virtual orbitals. They are of value in discussing excited states.

Roothaan's open shell method is more complicated than the closed shell method due to the fact that, in general, open shell wave functions involve a linear com-

bination of Slater determinants. Roothaan has, however, shown that in some cases the total energy can be written:[85,86,87]

$$\Gamma = 2\sum_{ic} H_{ic} + \sum_{kl} (2J_{kl} - K_{kl}) + f\left[2\sum_{m} H_{m} + f\sum_{mn} (2aJ_{mn} - bK_{mn}) + 2\sum_{km} (2J_{km} - K_{km})\right] \quad (31$$

where a, b, and f are numerical constants which depend on the open shell being considered. The fractional occupation of the open shall being considered is f and a and b differ for different states of the same configuration. When the variation principle is applied to this expression, with the usual orthogonality constraints applied, one obtains

$$\begin{aligned} F_c \phi_c &= \lambda_c \phi_c \\ F_o \phi_o &= \lambda_o \phi_o \end{aligned} \quad (32$$

and the total energy is given by

$$E = \sum_{\kappa} (H_\kappa + \lambda_\kappa) + f \sum_{m} (H_m + N_m)$$

The operators F_c and F_o are defined to be

$$F_c = H + 2J_c - K_c + 2J_o - K_o + 2\alpha L_o - \beta M_o \quad (33$$

$$F_o = H + 2J_c - K_c + 2aJ_o - bK_o + 2\alpha L_c - \beta M_c$$

where

$$\alpha = \frac{1-a}{1-f} \qquad \beta = \frac{1-b}{1-f}$$

An LCAO treatment of the open shell equations has been developed by Roothaan.[85] As usual these equations must be solved by an iterative procedure.

Appendix II

The POLYATOM system of programs has been discussed in a number of publications.[92, 94, 121] This set of programs employs Gaussian basis sets to compute MO-SCF wavefunctions and other properties derived from them. It does ab initio calculations in the sense that it computes all integrals and includes all electrons.

The system consists of a number of independent main programs. The output of each program is on tape and the input is from tape and cards. The integrals are listed in PA20A and PA20B and are evaluated in PA30A and PA30B. These integral routines will do one and two electron integrals over s, p, d, and f orbitals. PA40 performs a closed shell SCF calculation. Open shell calculations are performed by PA41, PA42, PA43, which do a variety of open shell methods. There are also special routines to do such things as population analysis

All the closed shell calculations reported here were done using PA40. The open shell calculations were done using PA42 which is based on Roothaan's double operator formalism.

TABLE 1

TOTAL ENERGIES OF H_n^+ CLUSTERS AT CALCULATED EQUILIBRIUM POSITIONS

Molecule	Energy
H_2	-1.1265
H_3^+	-1.2750
H_5^+	-2.4109
H_7^+	-3.5381
H_9^+	-4.6687
H_{11}^+	-5.7961
H_{13}^+	-6.9233
H_{15}^+	-8.0501

TABLE 2

THE CALCULATED BINDING ENERGY AND GEOMETRICAL

HYDROGEN CLUSTERS

$$E = E\ (H_n^+ - 2) + E\ (H_2) - E\ (H_n^+)$$

Molecule	E (Kcal/mole	(a.u.)[a4]	(a.u.)[b]	(a.u.)[c]
H_3^+(1)(2)	93.7			
H_5	6.0	3.7(3)		
H_7^+	.4	4.4		
H_9^+	2.5	4.5		
H_{11}^+	.6	4.5	5.8	
H_{13}^+	.6	4.5	6.0	
H_{15}^+	.3	4.5	6.0	7.5

---

(1) H-H distance in H_3^+ nucleating center held at 1.66 a.u. (For the case H_5^+ see Reference 65.)

(2) H-H distance in H_2 held at 1.40 a.u.

(3) All distances are from center of H_2 pairs to the center of H_3^+.

(4) For meaning of parameters a, b, and c, see Figure 1.

TABLE 3

DISTANCES AND ENERGIES FOR H_{11}^{+} [a]

A [b]	C [c]	E [d]
4.6	4.6	-5.79097
4.8	4.8	-5.79160
5.0	5.0	-5.79140
5.2	5.2	-5.79074
5.4	5.4	-5.78986
5.6	5.6	-5.78890
5.8	5.8	-5.78795
4.8	4.9	-5.79197
4.8	5.1	-5.79249
4.8	5.3	-5.79279
4.7	5.5	-5.79294

(a) This is for the first geometry of H_{11}^{+} discussed in Section II of text.

(b) A is the distance from center of H_3^{+} to center of any one of the three perpendicular H_2 pairs.

(c) C is the distance from center of H_3^{+} triangle to center of the H_2 pair whose axis lies along line joining center of triangle to center of H_2.

(d) E is energy in atomic units.

TABLE 4

DISTANCES AND ENERGIES FOR H_{11}^{+} (1)

a (2)	b	E (3)
4.4	4.4	-5.79190
4.6	4.6	-5.79339
4.8	4.8	-5.79362
5.0	5.0	-5.79307
4.6	4.8	-5.79446
4.6	5.0	-5.79514
4.6	5.2	-5.79554
4.6	5.4	-5.79577
4.6	5.6	-5.79588
4.6	5.8	-5.79592
4.6	6.0	-5.79590
4.6	6.6	-5.79574
4.8	5.8	-5.79508
4.5	5.8	-5.79608
4.4	5.8	-5.79599

(1) This is for second geometry described in Section II of text. See also Figure 1.

(2) See Figure 1 for meaning of parameters a and b.

(3) E is energy in atomic units.

TABLE 5

The exponents and contraction coefficients for the Gaussian basis set used in computations on H_{11}^{+}, HP1, HP2, and HP3 refer to protons in the H_3^{+} triangle. The other centers refer to the H_2 pairs.

GAUSSIAN FUNCTION SPECIFICATIONS

NUMBER OF PRIMITIVE GAUSSIANS = 44
NUMBER OF BASIS FUNCTIONS = 22

GAUSSIAN	FUNCTION	COMPONENT	CENTER	TYPE	EXPONENT	COEFFICIENT
1	1	1	HP1	S	.6531400	.0172300
2	1	2	HP1	S	2.8991500	.2312850
3	1	3	HP1	S	19.2406000	.0328250
4	2	1	HP2	S	.6531400	.0172300
5	2	2	HP2	S	2.8991500	.2312850
6	2	3	HP2	S	19.2406000	.0328250
7	3	1	HP3	S	.6531400	.0172300
8	3	2	HP3	S	2.8991500	.2312850
9	3	3	HP3	S	19.2406000	.0328250
10	4	1	H11	S	.6531400	.0172300
11	4	2	H11	S	2.8991500	.2312850
12	4	3	H11	S	19.2406000	.0328250
13	5	1	H12	S	.6531400	.0172300
14	5	2	H12	S	2.8991500	.2312850
15	5	3	H12	S	19.2406000	.0328250
16	6	1	H21	S	.6531400	.0172300
17	6	2	H21	S	2.8991500	.2312850
18	6	3	H21	S	19.2406000	.0328250
19	7	1	H22	S	.6531400	.0172300
20	7	2	H22	S	2.8991500	.2312850
21	7	3	H22	S	19.2406000	.0328250
22	8	1	H31	S	.6531400	.0172300
23	8	2	H31	S	2.8991500	.2312850
24	8	3	H31	S	19.2406000	.0328250
25	9	1	H32	S	.6531400	.0172300
26	9	2	H32	S	2.8991500	.2312850
27	9	3	H32	S	19.2406000	.0328250
28	10	1	H41	S	.6531400	.0172300
29	10	2	H41	S	2.8991500	.2312850
30	10	3	H41	S	19.2406000	.0328250
31	11	1	H42	S	.6531400	.0172300
32	11	2	H42	S	2.8991500	.2312850
33	11	3	H42	S	19.2406000	.0328250
34	12	1	HP1	S	.1775000	1.0000000
35	13	1	HP2	S	.1775000	1.0000000
36	14	1	HP3	S	.1775000	1.0000000
37	15	1	H11	S	.1775000	1.0000000
38	16	1	H12	S	.1775000	1.0000000
39	17	1	H21	S	.1775000	1.0000000
40	18	1	H22	S	.1775000	1.0000000
41	19	1	H31	S	.1775000	1.0000000
42	20	1	H32	S	.1775000	1.0000000
43	21	1	H41	S	.1775000	1.0000000
44	22	1	H42	S	.1775000	1.0000000

THE BASIS FUNCTIONS ARE LISTED IN STANDARD ORDER.

INTERNUCLEAR DISTANCES FROM GEOMETRY

CENTERS	A.U.	A.

TABLE 6

The coefficients of the basis functions in the MO's of the H_{11}^{+}. The Geometry is that of Figure 1 with a = 4.6 and b = 6.0. For exponents and contraction coefficients of the basis functions see Table 5.

H11+ AXIAL

MOLECULAR ORBITALS
ITERATION 10

ROW		1	2	3	4	5	6	7	8	9	10
1	A1	-1.1759207	1.00000								
1		.3009754	.3010605	.3010605	.0207458	.0207560	.0207174	.0207274	.0207174	.0207274	.0039646
		.0017556	.1348561	.1342878	.1342878	.0055428	.0056038	.0055289	.0055915	.0055289	.0055915
		-.0003325	.0029420								
2	A1	-.8160690	1.00000								
2		-.0290287	.0146941	.0146933	-.2585114	-.2586390	.1290043	.1290669	.1289970	.1290596	-.0000085
		-.0000000	-.1502935	.0750858	.0750815	-.2107437	-.2116255	.1051562	.1056025	.1051503	.1055966
		-.0000219	.0000022								
3	A1	-.8160138	1.00000								
3		.0000005	.0251392	-.0251396	.0000042	.0000042	.2237398	.2238487	-.2237440	-.2238529	.0000000
		.0000000	.0000024	.1295714	-.1295739	.0000034	.0000034	.1824236	.1831990	-.1824270	-.1832024
		.0000000	.0000000								
4	A1	-.7994927	1.00000								
4		.0694052	.0694949	.0694949	-.1828720	-.1829744	-.1832357	-.1833368	-.1832357	-.1833369	-.0110366
		-.0107749	.0177717	.0177589	.0177589	-.1598084	-.1599787	-.1601279	-.1603060	-.1601279	-.1603061
		-.0169442	-.0056275								
5	A1	-.7544238	1.00000								
5		.0070277	.0070374	.0070374	.0093329	.0085119	.0093322	.0085112	.0093322	.0085112	-.3185737
		-.3684353	.0003595	.0003811	.0003811	-.0018402	.0145006	-.0018434	.0145016	-.0018434	.0145016
		-.3415802	-.2195124								
6	A1	-.1207492									
6		.2816636	-.1409724	-.1409656	-.0709563	-.0710005	.0354454	.0354671	.0354437	.0354654	-.0000046
		-.0000064	1.5354189	-.7677613	-.7677245	-.1317930	-.1309413	.0658633	.0654333	.0658602	.0654301
		.0000058	-.0000159								
7	A1	-.1207137									
7		.0000039	.2441785	-.2441824	-.0000010	-.0000010	-.0613643	-.0614019	.0613652	.0614028	-.0000000
		-.0000000	.0000213	1.3296799	-1.3297012	-.0000018	-.0000018	-.1140374	-.1132957	.1140392	.1132975
		.0000000	-.0000000								
8	A1	.0318927									
8		-.0360536	-.0360690	-.0360690	.0464483	-.0642160	.0462843	-.0640496	.0462843	-.0640496	-.0095834
		-.0912503	.0207986	.0208341	.0208341	.8006379	-.7974839	.7988918	-.7957395	.7988918	-.7957394
		.8187685	-.7795997								
9	A1	.0593487									
9		.0002250	-.0000206	-.0000206	.1067550	-.1061777	-.0533854	.0531412	-.0533823	.0531382	-.0000179
		.0001242	.0004946	-.0003039	-.0003039	1.3257043	-1.3260071	-.6637182	.6638601	-.6636796	.6638216
		-.0012029	.0011637								
10	A1	.0593911									
10		-.0000000	-.0001421	.0001421	-.0000018	.0000018	-.0924325	.0919580	.0924343	-.0919598	.0000000
		-.0000000	-.0000000	-.0004620	.0004620	-.0000222	.0000222	-1.1486009	1.1488557	1.1486232	-1.1488780
		.0000001	-.0000001								

11	A1	.1066201									
11	.0903275	.0903679	.0903679	.0694165	-.0270535	.0694512	-.0270954	.0694512	-.0270954	-.0944309	
	.1215464	-.0605920	-.0606636	-.0606636	.4833817	-.4916034	.4840820	-.4922947	.4840820	-.4922947	
	-1.3813627	1.3838801									
12	A1	.4480602									
12	-.5493617	-.5497096	-.5497096	-.1835384	-.1910781	-.1834904	-.1910269	-.1834904	-.1910269	-.2552192	
	-.0777333	.4676096	.4681315	.4681315	.1048618	.0864480	.1047914	.0863697	.1047914	.0863697	
	-.2212393	.4732111									
13	A1	.7043483									
13	-.0828543	.0416762	.0416745	-.6717197	-.6725759	.3348690	.3349510	.3348553	.3349373	.0019114	
	.0018933	-.4513490	.2252838	.2252746	.6465092	.6462915	-.3220613	-.3220995	-.3220482	-.3220863	
	-.0016467	-.0017322									
14	A1	.7044245									
14	.0000610	.0720688	-.0720698	.0000079	.0000080	.5811449	.5816829	-.5811528	-.5816907	-.0000001	
	-.0000001	.0000053	.3904049	-.3904102	-.0000076	-.0000076	-.5591706	-.5590645	.5591782	.5590720	
	.0000001	.0000001									
15	A1	.7102501									
15	.0541345	.0545969	.0545969	.1091570	.2043370	.1119341	.2070851	.1119342	.2070852	-.7480727	
	-.7663922	-.0346648	-.0329838	-.0329838	-.1579742	-.1192735	-.1606499	-.1218842	-.1606499	-.1218843	
	.6879857	.6639242									
16	A1	.7664937									
16	.3588625	.3590323	.3590323	-.4275879	-.3886704	-.4284682	-.3895613	-.4284682	-.3895613	-.1727919	
	-.2542104	-.3968651	-.3970960	-.3970961	.4207335	.4267296	.4215977	.4276169	.4215977	.4276169	
	.2708683	.1282876									
17	A1	.9551728									
17	.0000053	-1.0660254	1.0660201	-.0000003	-.0000003	.0579195	.0577797	-.0579192	-.0577794	.0000000	
	-.0000000	-.0000084	1.6888089	-1.6888005	.0000009	.0000009	-.1777630	-.1776960	.1777621	.1776951	
	.0000000	.0000000									
18	A1	.9552646									
18	-1.2311500	.6152897	.6152989	.0668115	.0666334	-.0333610	-.0332965	-.0333615	-.0332970	-.0000004	
	.0000393	1.9500599	-.9748171	-.9748316	-.2051863	-.2050999	.1025396	.1025093	.1025411	.1025109	
	-.0000489	-.0000476									
19	A1	1.2416772									
19	-.0242724	-.0242555	-.0242555	.5811319	-.5819954	.5776480	-.5785164	.5776480	-.5785163	.4649991	
	-.5988903	.0269117	.0268843	.0268843	-.6827734	.6782179	-.6784736	.6739260	-.6784735	.6739259	
	-.4960923	.6202530									
20	A1	1.2704837									
20	.0002066	.0000402	.0000402	.9341265	-.9337094	-.4690482	.4688451	-.4690326	.4688295	-.0015714	
	.0018334	-.0002093	-.0000527	-.0000527	-1.1415068	1.1411975	.5730198	-.5728375	.5730008	-.5728185	
	.0017736	-.0026291									
21	A1	1.2705987									
21	-.0000000	-.0000958	.0000958	-.0000089	.0000089	-.8101180	.8097628	.8101270	-.8097719	.0000000	
	-.0000001	.0000000	.0000908	-.0000908	.0000109	-.0000109	.9898410	-.9895592	-.9898521	.9895702	
	-.0000001	.0000001									
22	A1	1.3712098									
22	-.0861408	-.0860967	-.0860967	-.3143282	.3137150	-.3148679	.3142572	-.3148679	.3142572	1.0614366	
	-.9762846	.0934845	.0934160	.0934160	.4293263	-.4480966	.4299754	-.4487362	.4299755	-.4487362	
	-1.3762272	1.2821394									

TABLE 7

Exponents of Gaussian basis functions used in $BeHe^{2+}$ calculation described in Section III.

*** GAUSSIAN FUNCTION SPECIFICATIONS ***

NUMBER OF PRIMITIVE GAUSSIANS = 23
NUMBER OF BASIS FUNCTIONS = 23

GAUSSIAN	FUNCTION	COMPONENT	CENTER	TYPE	EXPONENT	COEFFICIENT
1	1	1	HEPP	S	96.7296000	1.0000000
2	2	1	HEPP	S	14.6094000	1.0000000
3	3	1	HEPP	S	3.3042410	1.0000000
4	4	1	HEPP	S	.8730980	1.0000000
5	5	1	HEPP	S	.2445280	1.0000000
6	6	1	BEPP	S	1.3543100	1.0000000
7	7	1	BEPP	S	532.2850000	1.0000000
8	8	1	BEPP	S	117.7990000	1.0000000
9	9	1	BEPP	S	32.6562000	1.0000000
10	10	1	BEPP	S	3.6682600	1.0000000
11	11	1	BEPP	S	3630.3800000	1.0000000
12	12	1	BEPP	S	10.4801000	1.0000000
13	13	1	BEPP	S	.0524060	1.0000000
14	14	1	BEPP	S	.1502300	1.0000000
15	15	1	BEPP	S	.3890500	1.0000000
16	16	1	BEPP	Z	.0330000	1.0000000
17	17	1	BEPP	Z	1.9600000	1.0000000
18	18	1	BEPP	Z	8.3500000	1.0000000
19	19	1	BEPP	Z	.5700000	1.0000000
20	20	1	BEPP	Z	.2120000	1.0000000
21	21	1	BEPP	Z	.0820000	1.0000000
22	22	1	HEPP	Z	.5400000	1.0000000
23	23	1	HEPP	Z	2.7000000	1.0000000

THE BASIS FUNCTIONS ARE LISTED IN STANDARD ORDER

*** RENORMALIZATION ***

GAUSSIAN	FUNCTION	COMPONENT	CENTER	TYPE	L	M	N	EXPONENT	COEFFICIENT
1	1	1	1	1	0	0	0	96.7296000	1.0000000
2	2	1	1	1	0	0	0	14.6094000	1.0000000
3	3	1	1	1	0	0	0	3.3042410	1.0000000
4	4	1	1	1	0	0	0	.8730930	1.0000000
5	5	1	1	1	0	0	0	.2445280	1.0000000
6	6	1	2	1	0	0	0	1.3543100	1.0000000
7	7	1	2	1	0	0	0	532.2850000	1.0000000
8	8	1	2	1	0	0	0	117.7990000	1.0000000
9	9	1	2	1	0	0	0	32.6562000	1.0000000
10	10	1	2	1	0	0	0	3.6682600	1.0000000
11	11	1	2	1	0	0	0	3630.3800000	1.0000000
12	12	1	2	1	0	0	0	10.4801000	1.0000000
13	13	1	2	1	0	0	0	.0524060	1.0000000
14	14	1	2	1	0	0	0	.1502300	1.0000000
15	15	1	2	1	0	0	0	.3890500	1.0000000
16	16	1	2	4	0	0	1	.0330000	1.0000000
17	17	1	2	4	0	0	1	1.9600000	1.0000000
18	18	1	2	4	0	0	1	8.3500000	1.0000000
19	19	1	2	4	0	0	1	.5700000	1.0000000
20	20	1	2	4	0	0	1	.2120000	1.0000000
21	21	1	2	4	0	0	1	.0820000	1.0000000

TABLE 8

INTERNUCLEAR DISTANCES AND ENERGIES IN $Be^{2+}He$

(a) R	(b) E
1.5	-16.21327
2.5	-16.49838
2.6	-16.50008
2.67	-16.50055
2.7	-16.50060
2.71	-16.50061
2.73	-16.50059
2.75	-16.50054
2.8	-16.50030
2.9	-16.49941
3.1	-16.49660
3.7	-16.48673
(c)	-16.47082

(a) R is distance in atomic units.

(b) E is energy in atomic units.

(c) Sum of separated atom and ion energies. Note that Be^{2+} energy is -13.61093, and He energy is -2.85989.

TABLE 9

DISSOCIATION ENERGIES AND BOND LENGTHS OF VARIOUS MOLECULE IONS

Molecule-Ion	Bond Length (atomic units)	Calculated Dissociation Energy (kcal/mole)	Symmetry	State
$BeHe^{2+}$	2.71	18.6[a]	$C_{\infty v}$	$^1\Sigma^+$
$Be^{2+}(He)_2$	2.72[c]	17.7[b]	$D_{\infty h}$	$^1\Sigma^+$
Be+He	6.4	0.12	$C_{\infty v}$	$^2\Sigma^+$
He_3^{2+}	----	unstable	----	----
$He^{2+}(H_2)_2$	----	unstable	----	----
HeC^{2+}	3.26	9.3	$C_{\infty v}$	$^1\Sigma^+$
HeC^+	4.89	0.55	$C_{\infty v}$	$^2\Pi$
H_{11}^+	See Table 1	0.6	C_{3v}	$^1A_1$

(a) Relative to dissociation into Be^{2+} and He.

(b) Relative to dissociation into $HeBe^{2+}$ and He.

(c) Be^{2+} to He distance.

TABLE 10

Coefficients of basis functions in MO's of $BeHe^{2+}$ at internuclear separation of 2.71 a.u. For exponents of basis functions, see Table 7.

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MOLECULAR ORBITALS
ITERATION 5

ROW		1	2	3	4	5	6	7	8	9	10
1	A1	-5.6166812	1.00000								
1		-.0000162	-.0001366	-.0003690	-.0009663	-.0006222	-.3392802	-.0042258	-.0224221	-.0870465	-.4323415
		-.0005271	-.2420451	-.0017099	.0079499	-.0357945	-.0000592	.0010288	.0001135	.0000705	-.0000142
		.0002282	.0002972	.0001288							
2	A1	-1.6755721	1.00000								
2		-.0075670	-.0554764	-.2137191	-.5037783	-.3388656	.0456565	.0002185	.0012027	.0045750	.0269153
		.0000278	.0142989	.0127527	-.0268439	-.0571464	-.0022682	-.0108832	-.0024905	-.0559314	-.0242500
		.0192015	.0634426	.0043764							
3	A1	-.6155058									
3		.0011766	.0084940	.0352075	.0839996	.1636699	.1781868	.0008330	.0045109	.0176571	.1116519
		.0001046	.0538145	-.2073246	-.8384053	-.0690199	.0058550	.0196017	.0036875	.0793635	.1265886
		.0824856	-.0041838	.0029357							
4	A1	-.3749413									
4		.0027862	.0188593	.0882510	.1685478	.7891802	.0604195	.0002977	.0015868	.0063743	.0421845
		.0000369	.0187436	-.1176512	-.6216332	.0494300	-.0040302	-.0643283	-.0105493	-.2031836	-.6686021
		-.5503932	-.0327226	.0128398							
5	A1	-.2557997									
5		.0001487	.0011519	.0045732	.0143567	.0156059	-.0757142	-.0004842	-.0023897	-.0106571	-.0762437
		-.0000570	-.0270781	-1.5553748	1.4433627	-.0915690	-.4633157	.0194968	.0031543	.0682834	.2044759
		-.1057171	-.0418362	-.0080154							
6	A1	-.2286794									
6		-.0000616	.0003721	-.0041661	.0196930	-.0997146	.0481652	.0003019	.0014943	.0066390	.0473492
		.0000356	.0169583	.9534405	-.8767906	.0540838	-.9365086	.0341586	.0058277	.1334035	.3284759
		.1197914	-.0178553	-.0030271							
7	A1	-.0369444									
7		-.0000871	.0008071	-.0072240	.0372304	-.2762693	.0097173	-.0000461	-.0001202	-.0011796	-.0115455
		-.0000037	-.0005127	-.0773361	.2905460	-.0884374	-1.5190360	-.0710804	-.0077940	-.1340728	-1.0667796
		2.5334822	.0462932	.0072061							
8	A1	.3923472									
8		.0034763	.0465856	.0493693	1.0211938	-2.1519670	.3930245	.0005324	.0042256	.0092975	.0208611
		.0000881	.0612751	-.2183512	2.0983360	-1.5667313	.1813317	-.0292652	-.0115449	-.4944724	1.1057952
		.0092278	.2193123	-.0127917							
9	A1	.4492165									
9		-.0014071	-.0265344	.0024133	-.6533624	.7773416	.7497792	.0007653	.0069624	.0119829	-.0092565
		.0001407	.1056399	-1.3665885	3.0614416	-2.7997519	.0760001	.0215632	.0042042	.0841579	.2507196
		-.4677507	.3608112	.0020971							
10	A1	.6938879									
10		-.0004750	-.0155724	.0198831	-.4320528	.1901648	-.3404409	-.0003631	-.0032474	-.0057915	.0001084
		-.0000658	-.0491511	.0771140	-.5290751	1.0085122	.6722395	-.0152597	-.0248994	-1.2997434	2.7323374
		-2.0349574	.7176324	-.0100049							

11	M1	.9305727								
11	-.0012367	-.0130527	-.0106034	-.5637328	1.1135064	.3493362	.0002659	.0028152	.0035671	-.0196012
	.0000551	.0448687	-.1449709	.0324201	-.9273799	.1788300	-.0297816	-.0242617	-1.0072659	.4729508
	-.5585708	-1.1135522	.0257620							
12	A1	3.8393129								
12	.0028685	-.0004729	.2004950	-.3388736	.2580374	-.0714235	.0001345	.0001671	.0038473	.0535474
	.0000079	-.0020673	.0131328	-.1287794	.0208836	.2435994	1.4575422	-.0013397	-1.8662846	1.3145861
	-.7445871	-.2073727	.0859797							
13	A1	4.2486331								
13	-.0042830	.0002552	-.3030461	.3748784	-.2259729	-3.5462437	.0046421	.0026441	.1383720	2.0673935
	.0002231	-.1390999	.4942594	-1.6490564	2.9064531	.0211359	-.0026293	-.0000170	.0215984	.1003619
	-.0412561	.1818301	-.0656293							
14	A1	4.7168777								
14	.0215058	-.0146918	1.5992537	-2.1034172	1.1923290	-.7769605	.0009078	.0001906	.0276512	.4277400
	.0000384	-.0338762	-.0937496	-.4649535	.6507981	.0272275	-.2037573	-.0004210	.2206894	-.0502147
	-.2925251	.0462833	-.1023284							
15	A1	6.0806247								
15	-.0016547	-.0014103	-.1409994	.2629255	-.4426495	.1918658	-.0002834	-.0009919	-.0073161	-.1197748
	-.0000267	-.0082007	-.0824496	.4076994	-.0969505	.0345065	.1021036	.0128807	-.0388125	.3773938
	-.1144169	.7669732	-1.1711380							
16	A1	18.6659511								
16	-.0000038	-.0048717	-.0123365	.0375435	-.0323648	2.7594493	-.0015082	.0878552	-.1906152	-3.9420416
	.0012632	2.4528939	-.2121932	.7902359	-1.4519906	-.0188434	-.0729242	.0924070	.0486746	-.0692648
	.0634197	-.0362876	-.0146833							
17	A1	19.0613628								
17	-.0000937	.0110326	.0104891	-.0065199	-.0000475	-.2296925	.0001142	-.0064897	.0142241	.3040521
	-.0000946	-.1834514	.0101860	-.0592413	.1372744	-.0881653	-1.0853714	1.2647876	.7693558	-.4980897
	.2551231	.0365167	.0199291							
18	A1	25.8022781								
18	.0263261	-1.5364826	1.7020348	-1.0356697	.4987848	-.0713753	.0000097	-.0005744	.0013261	.0505358
	-.0000082	-.0201115	-.0681669	-.0774128	.0534990	.0183170	-.0302254	.0152319	.0141372	.0150596
	-.1357081	-.0224282	.0117349							
19	A1	68.8320746								
19	.0001824	.0030617	-.0115776	.0198160	-.0152492	1.4143244	-.0423885	.1758505	-2.3096439	-2.6120899
	.0009114	3.3852225	-.1030596	.3818982	-.7016060	-.0061000	.0038264	-.0013015	-.0042530	-.0163994
	.0220025	-.0207018	-.0049417							
20	A1	170.9876848								
20	1.2645059	-1.0428346	.6310643	-.3501242	.1705558	-.0199915	-.0000317	.0005114	.0011456	.0124883
	.0000053	-.0052250	-.0242020	-.0246191	.0152449	.0070080	-.0068822	.0019277	.0014530	.0079262
	-.0486669	-.0071549	.0030079							
21	A1	259.9300834								
21	.0007877	-.0019074	.0056275	-.0093353	.0070853	-.6667143	.1245605	-1.9474950	2.5262031	1.2587222
	-.0145763	-1.9527193	.0498099	-.1836169	.3349784	.0029777	-.0017210	.0005128	.0020017	.0081013
	-.0106896	.0102933	.0020341							
22	A1	1141.2742207								
22	.0001612	-.0006739	.0023868	-.0040561	.0030793	-.2920728	1.5695739	-1.6860434	1.2270569	.5437038
	-.0619955	-.8432454	.0221924	-.0816169	.1483882	.0013292	-.0007542	.0002178	.0008912	.0036316
	-.0047602	.0046340	.0008551							

TABLE 11

Exponents of Gaussian basis functions used in calculations on He_2Be^{2+} as described in Section III of the text.

*** GAUSSIAN FUNCTION SPECIFICATIONS ***

NUMBER OF PRIMITIVE GAUSSIANS = 30
NUMBER OF BASIS FUNCTIONS = 30

GAUSSIAN	FUNCTION	COMPONENT	CENTER	TYPE	EXPONENT	COEFFICIENT
1	1	1	HEPP1	S	.2445280	1.0000000
2	2	1	HEPP1	S	.8730980	1.0000000
3	3	1	HEPP1	S	3.3042410	1.0000000
4	4	1	HEPP1	S	14.6094000	1.0000000
5	5	1	HEPP1	S	96.7296000	1.0000000
6	6	1	HEPP12	S	.2445280	1.0000000
7	7	1	HEPP12	S	.8730980	1.0000000
8	8	1	HEPP12	S	3.3042410	1.0000000
9	9	1	HEPP12	S	14.6094000	1.0000000
10	10	1	HEPP12	S	96.7296000	1.0000000
11	11	1	BEPP	S	1.3543100	1.0000000
12	12	1	BEPP	S	532.2800000	1.0000000
13	13	1	BEPP	S	117.7990000	1.0000000
14	14	1	BEPP	S	32.6562000	1.0000000
15	15	1	BEPP	S	3.6682600	1.0000000
16	16	1	BEPP	S	3630.3800000	1.0000000
17	17	1	BEPP	S	10.4881000	1.0000000
18	18	1	BEPP	S	.0524060	1.0000000
19	19	1	BEPP	S	.1502300	1.0000000
20	20	1	BEPP	S	.3890500	1.0000000
21	21	1	BEPP	Z	.0330000	1.0000000
22	22	1	BEPP	Z	1.9600000	1.0000000
23	23	1	BEPP	Z	8.3500000	1.0000000
24	24	1	BEPP	Z	.5700000	1.0000000
25	25	1	BEPP	Z	.2120000	1.0000000
26	26	1	BEPP	Z	.0820000	1.0000000
27	27	1	HEPP1	Z	.5400000	1.0000000
28	28	1	HEPP1	Z	2.7000000	1.0000000
29	29	1	HEPP12	Z	.5400000	1.0000000
30	30	1	HEPP12	Z	2.7000000	1.0000000

THE BASIS FUNCTIONS ARE LISTED IN STANDARD ORDER

INTERNUCLEAR DISTANCES FROM GEOMETRY

CENTERS	A.U.	A.
HEPP1 - HEPP12	5.440000	2.878685
HEPP1 - BEPP	2.720000	1.439342
HEPP12 - BEPP	2.720000	1.439342

NUCLEAR REPULSION ENERGY = 6.61764706 A.U.

PSEUDO END-OF-FILE MARKS USED
PSEUDO END-OF-FILE MARKS USED

START 1-ELEC. INTS ... ELAPSED CP TIME IS .284 SECONDS

TABLE 12

ENERGIES AND DISTANCES IN $Be^{2+}(He)_2$ [a]

R_1 [b]	R_2	E [c]
1.7	1.7	-19.08860
2.3	2.3	-19.36625
2.5	2.5	-19.38405
2.65	2.65	-19.38847
2.71	2.71	-19.38886
2.72	2.72	-19.38887
2.73	2.73	-19.38886
2.75	2.75	-19.38879
2.70	2.72	-19.38885
2.72	2.73	-19.38886
2.72	2.71	-19.38886
2.74	2.72	-19.38885

(a) For linear symmetric case with symmetry $D_{\infty h}$.

(b) Distances in atomic units.

(c) Energy in atomic units.

TABLE 13

Coefficients of basis functions in MO's of $(He)_2Be^{2+}$. Both Be - He distances are 2.72 a.u. For exponents of basis functions see Table 11.

HEPP D SYMMETRY 7/71

MOLECULAR ORBITALS
ITERATION 5

ROW	1	2	3	4	5	6	7	8	9	10
1	A1 -5.5698953	1.00000								
1	-.0005605	-.0009774	-.0003545	-.0001373	-.0000158	-.0005605	-.0009774	-.0003545	-.0001373	-.0000158
	-.3391242	-.0042244	-.0224146	-.0870124	-.4321458	-.0005269	-.2419429	-.0017373	.0083278	-.0366470
	-.0000000	.0000000	-.0000000	-.0000000	.0000000	-.0000000	.0003194	.0001132	-.0003194	-.0001132
2	A1 -1.6629482	1.00000								
2	-.2328604	-.3544767	-.1517319	-.0390840	-.0053578	.2328604	.3544767	.1517319	.0390840	.0053578
	.0000000	.0000000	.0000000	.0000000	.0000000	.0000000	.0000000	-.0000000	.0000000	-.0000000
	-.0060251	-.0139022	-.0034871	-.0757759	-.0525854	.0342725	.0355656	.0040570	.0355656	.0040570
3	A1 -1.6559440	1.00000								
3	-.2424632	-.3579854	-.1508485	-.0393905	-.0053521	-.2424632	-.3579854	-.1508485	-.0393905	-.0053521
	.0609817	.0003657	.0016629	.0064276	.0382837	.0000385	.0196205	.0150740	-.0335654	-.0749343
	.0000000	.0000000	.0000000	.0000000	.0000000	-.0000000	.0488772	.0022765	-.0488772	-.0022765
4	A1 -.5246834									
4	.3536351	.1299279	.0587772	.0136412	.0019279	.3536351	.1299279	.0587772	.0136412	.0019279
	.1768384	.0008479	.0045618	.0180282	.1154878	.0001060	.0542601	-.2956351	-1.0793695	-.0032486
	-.0000000	-.0000000	.0000000	.0000000	.0000000	.0000000	-.0132538	.0063842	.0132538	-.0063842
5	A1 -.2501581									
5	-.0062477	-.0026946	-.0016400	-.0003250	-.0000464	-.0062477	-.0026946	-.0016400	-.0003250	-.0000464
	.0858561	.0025706	.0028045	.0125744	.0901374	.0000671	.0316487	1.8113918	-1.7134313	.1270053
	.0000000	.0000000	.0000000	.0000000	.0000000	.0000000	.0281323	.0054632	-.0281323	-.0054632
6	A1 -.2446220									
6	-.2511577	-.0911279	-.0331196	-.0081336	-.0010977	.2511577	.0911279	.0331196	.0081336	.0010977
	-.0000000	-.0000000	-.0000000	-.0000000	-.0000000	-.0000000	-.0000000	-.0000000	.0000000	-.0000000
	.9392188	-.0015035	-.0006330	-.0265755	-.0028691	.2892193	.0288452	.0018051	.0288452	.0018051
7	A1 -.2371478									
7	.7078090	.1553613	.0727104	.0160239	.0023138	-.7078090	-.1553613	-.0727104	-.0160239	-.0023138
	.0000000	.0000000	.0000000	.0000000	.0000000	.0000000	.0000000	.0000000	-.0000000	.0000000
	.3387716	-.0896161	-.0139446	-.2701992	-1.0161463	-.6052943	.0094290	.0128950	.0094290	.0128950
8	A1 -.0413453									
8	-.3946492	-.0035402	-.0225176	-.0027207	-.0005793	.3946492	.0035402	.0225176	.0027207	.0005793
	-.0000000	-.0000000	-.0000000	-.0000000	-.0000000	-.0000000	-.0000000	-.0000000	.0000000	.0000000
	-1.6112701	-.0531798	-.0053911	-.0725220	-.9372019	2.8474478	.0206298	.0067066	.0206298	.0067066
9	A1 .3962126									
9	-1.3736032	.8575574	.0269172	.0384707	.0026040	-1.3736032	.8575574	.0269172	.0384707	.0026040
	.2209664	.0003868	.0028048	.0071694	.0275109	.0000598	.0392054	.3851915	.9457719	-.7644494
	.0000000	.0000000	-.0000000	-.0000000	.0000000	-.0000000	-.1124496	-.0031515	.1124496	.0031515
10	A1 .4092415									
10	-.1039441	-.1139855	.0249165	-.0028049	.0003208	-.1039441	-.1139855	.0249165	-.0028049	.0003208
	.7310338	.0008109	.0070621	.0131750	.0030488	.0001441	.1056203	-1.3613007	3.5979782	-2.8893532
	.0000000	.0000000	.0000000	.0000000	-.0000000	-.0000000	.3908037	-.0019841	-.3908037	.0019841

11	A1	.5337455								
11	-2.1043272	.7631717	.0257037	.0323969	.0022477	2.1043272	-.7631717	-.0257037	-.0323969	-.0022477
	.0000000	.0000000	.0000000	-.0000000	-.0000000	.0000000	.0000000	-.0000000	.0000000	-.0000000
	.0328596	-.0399114	-.0190962	-.8353576	1.7456947	.8104007	.0456819	-.0090893	.0456819	-.0090893
12	A1	.7671386								
12	.4496258	-.6299781	.0094840	-.0225217	-.0010741	-.4496258	.6299781	-.0094840	.0225217	.0010741
	-.0000000	-.0000000	-.0000000	-.0000000	-.0000000	-.0000000	-.0000000	.0000000	-.0000000	.0000000
	.7389386	.0088377	-.0268992	-1.4738932	3.1461329	-2.4257884	.4314486	-.0000192	.4314486	-.0000192
13	A1	.8234455								
13	.6638645	-.3824151	-.0243369	-.0140337	-.0012573	.6638645	-.3824151	-.0243369	-.0140337	-.0012573
	.6550073	.0005224	.0054470	.0071225	-.0348846	.0001070	.0861954	-.3693931	.7287957	-1.8901836
	.0000000	-.0000000	-.0000000	-.0000000	.0000000	-.0000000	-.7685858	.0171468	.7685858	-.0171468
14	A1	1.3303817								
14	1.8461664	-.4624153	-.0067030	-.0131299	-.0008621	-1.8461664	.4624153	.0067030	.0131299	.0008621
	-.0000000	.0000000	-.0000000	.0000000	.0000000	.0000000	-.0000000	.0000000	-.0000000	.0000000
	-.0076608	-.0669919	-.0176428	-.5004057	-1.7858752	-.3206666	-1.1812302	.0090201	-1.1812302	.0090201
15	A1	3.9144179								
15	.4868205	-.3839643	.2116651	-.0013013	.0029880	-.4868205	.3839643	-.2116651	.0013013	-.0029880
	-.0000000	.0000000	-.0000000	.0000000	.0000000	.0000000	-.0000000	.0000000	-.0000000	.0000000
	.2246643	1.4538082	-.0017103	-1.8784147	.9482174	-.7693666	-.2948899	.0582108	-.2948899	.0582108
16	A1	4.2878186								
16	.1820061	-.3373291	.2681988	-.0000659	.0037790	.1820061	-.3373291	.2681988	-.0000659	.0037790
	3.5156875	-.0045881	-.0025775	-.1368097	-2.0449109	-.0002199	.1383307	-.4814856	1.5942633	-2.9073645
	.0000000	.0000000	.0000000	-.0000000	-.0000000	-.0000000	-.1581893	.0707676	.1581893	-.0707676
17	A1	4.6695256								
17	-.7703616	1.4486453	-1.1175728	.0106091	-.0151218	-.7703616	1.4486453	-1.1175728	.0106091	-.0151218
	.9471107	-.0011276	-.0001725	-.0344112	-.5282977	-.0000467	.0431899	.1168788	.5445702	-.7578924
	-.0000000	.0000000	-.0000000	-.0000000	.0000000	.0000000	-.0077557	.0939398	.0077557	-.0939398
18	A1	4.8675324								
18	1.1091080	-1.5895412	1.1568546	-.0101508	.0153420	-1.1091080	1.5895412	-1.1568546	.0101508	-.0153420
	.0000000	-.0000000	.0000000	-.0000000	-.0000000	-.0000000	.0000000	.0000000	.0000000	-.0000000
	.0894367	-.3009708	-.0015604	.3347300	-.1559463	-.6500633	.0339024	-.0710920	.0339024	-.0710920
19	A1	6.0461988								
19	.2716507	-.2424055	.1372170	.0010632	.0016220	.2716507	-.2424055	.1372170	.0010632	.0016220
	-.3454788	.0004730	.0014572	.0125672	.2055432	.0000414	.0095200	-.1061658	-.4917968	.1828525
	-.0000000	.0000000	-.0000000	-.0000000	-.0000000	-.0000000	-.4864126	.8168582	.4864126	-.8188582
20	A1	6.3911267								
20	-.8268773	.2752791	-.1159804	-.0005080	-.0013030	.8268773	-.2752791	.1159804	.0005080	.0013030
	-.0000000	.0000000	.0000000	.0000000	.0000000	.0000000	.0000000	.0000000	-.0000000	.0000000
	.0347370	.0661051	.0168748	.0280727	1.0572157	-.0064607	.7866243	-.8587071	.7866243	-.8587071
21	A1	18.7361965								
21	-.0262989	.0295259	-.0118897	-.0034564	-.0000276	-.0262989	.0295259	-.0118897	-.0034564	-.0000276
	2.7859582	-.0015134	.0881047	-.1912424	-3.9626496	.0012868	2.4616118	-.2042617	.7949983	-1.4763111
	-.0000000	-.0000000	.0000000	.0000000	-.0000000	.0000000	-.0288939	-.0182661	.0288939	.0182661
22	A1	19.1425343								
22	-.0227557	-.0043241	.0088948	.0133600	-.0001432	.0227557	.0043241	-.0088948	-.0133600	.0001432
	-.0000000	.0000000	-.0000000	.0000000	.0000000	-.0000000	-.0000000	.0000000	-.0000000	.0000000
	-.0782184	-1.0980393	1.2695547	.7864041	-.4426176	.2271296	.0541777	.0118850	.0541777	.0118850

```
23  A1        25.7748125
23   -.3199071     .7145127  -1.1958948   1.0852434   -.0186201   -.3199071     .7145127  -1.1958948   1.0852434   -.0186201
      .0755076    -.0000154     .0005962    -.0015395    -.0528057     .0000084     .0204990     .0832179     .0817741    -.0429361
      .0000000     .0000000     .0000000    -.0000000     .0000000    -.0000000     .0278368    -.0119010    -.0278368     .0119010

24  A1        25.9357160
24   -.4861224     .7868480  -1.2241845   1.0897053   -.0186084     .4861224    -.7868480   1.2241845  -1.0897053     .0186084
      .0000000     .0000000     .0000000    -.0000000    -.0000000    -.0000000     .0000000    -.0000000     .0000000    -.0000000
     -.0474030     .0492805    -.0258126    -.0291105     .0362555     .2958635     .0258183    -.0106970     .0258183    -.0106970

25  A1        68.9007971
25    .0121452    -.0148381     .0091679    -.0022742    -.0001219     .0121452    -.0148381     .0091679    -.0022742    -.0001219
     -1.4237254     .0423900    -.1758684    2.3101769    2.6184287    -.0009114   -3.3879009     .0990784    -.3829572     .7111963
      .0000000    -.0000000     .0000000     .0000000     .0000000    -.0000000     .0158767     .0057935    -.0158767    -.0057935

26  A1       170.9696597
26   -.1090898     .2413963    -.4433635     .7364263    -.8940133    -.1090898     .2413963    -.4433635     .7364263    -.8940133
      .0217098     .0000320    -.0005215    -.0012164    -.0136687    -.0000054     .0055803     .0295097     .0257325    -.0117557
      .0000000    -.0000000     .0000000     .0000000    -.0000000    -.0000000     .0088348    -.0031432    -.0088348     .0031432

27  A1       171.6976672
27   -.1665011     .2660815    -.4539372     .7399443    -.8944751     .1665011    -.2660815     .4539372    -.7399443     .8944751
      .0000000     .0000000    -.0000000    -.0000000    -.0000000    -.0000000     .0000000     .0000000     .0000000    -.0000000
     -.0173924     .0108519    -.0031492    -.0043016     .0084018     .1047630     .0086424    -.0028605     .0086424    -.0028605

28  A1       259.9990185
28    .0056504    -.0069726     .0044882    -.0014378     .0005805     .0056504    -.0069726     .0044882    -.0014378     .0005805
     -.6712427     .1245622   -1.9476077    2.5268170    1.2618557    -.0145763   -1.9543250     .0478706    -.1840681     .3396569
     -.0000000    -.0000000     .0000000     .0000000     .0000000     .0000000     .0079522     .0024306    -.0079522    -.0024306

29  A1      1141.3423210
29    .0024609    -.0030279     .0019168    -.0005157     .0001207     .0024609    -.0030279     .0019168    -.0005157     .0001207
     -.2943679    1.5695915   -1.6861494    1.2273623     .5450660    -.0619955    -.8439463     .0213266    -.0818045     .1504720
     -.0000000     .0000000     .0000000    -.0000000    -.0000000    -.0000000     .0035879     .0010302    -.0035879    -.0010302

30  A1      7022.1887898
30   -.0008948     .0011015    -.0006977     .0001843    -.0000398    -.0008948     .0011015    -.0006977     .0001843    -.0000398
      .1068093    -.9767910     .6274824    -.4299733    -.1964679    1.2527429     .2999685    -.0077929     .0298717    -.0548866
     -.0000000    -.0000000     .0000000     .0000000     .0000000     .0000000    -.0013160    -.0003711     .0013160     .0003711

                                                  END OFCALCULATION   ...  ELAPSED CP TIME IS     82.491   SECONDS
```

TABLE 14

ENERGIES AND DISTANCES IN $HeBe^+$

(a) R	(b) E
2.8	-17.12160
3.0	-17.12480
3.2	-17.12712
3.6	-17.13058
4.0	-17.13316
5.0	-17.13637
6.2	-17.13705
6.4	-17.13706
6.5	-17.13705
6.6	-17.13705
6.8	-17.13704
7.2	-17.13701
∞ (c)	-17.13681

(a) R is distance in atomic units.

(b) E is energy in atomic units.

(c) Sum of separated atom and ion energies. Note that Be^+ energy is -14.27691 and He energy is 2.85989.

TABLE 15

Exponents of Gaussian basis functions in basis set of $HeBe^{+}$.

*** GAUSSIAN FUNCTION SPECIFICATIONS ***

NUMBER OF PRIMITIVE GAUSSIANS = 23
NUMBER OF BASIS FUNCTIONS = 23

GAUSSIAN	FUNCTION	COMPONENT	CENTER	TYPE	EXPONENT	COEFFICIENT
1	1	1	HE	S	.2445280	1.0000000
2	2	1	HE	S	.8739980	1.0000000
3	3	1	HE	S	3.3042410	1.0000000
4	4	1	HE	S	14.6094000	1.0000000
5	5	1	HE	S	96.7296000	1.0000000
6	6	1	BE	S	1.3543100	1.0000000
7	7	1	BE	S	532.2800000	1.0000000
8	8	1	BE	S	117.7990000	1.0000000
9	9	1	BE	S	32.6562000	1.0000000
10	10	1	BE	S	3.6682600	1.0000000
11	11	1	BE	S	3630.3800000	1.0000000
12	12	1	BE	S	10.4891000	1.0000000
13	13	1	BE	S	.0524060	1.0000000
14	14	1	BE	S	.1502300	1.0000000
15	15	1	BE	S	.3690500	1.0000000
16	16	1	BE	Z	1.9600000	1.0000000
17	17	1	BE	Z	.0330000	1.0000000
18	18	1	BE	Z	8.3500000	1.0000000
19	19	1	BE	Z	.5700000	1.0000000
20	20	1	BE	Z	.2120000	1.0000000
21	21	1	BE	Z	.0020000	1.0000000
22	22	1	HE	Z	.5400000	1.0000000
23	23	1	HE	Z	2.7000000	1.0000000

THE BASIS FUNCTIONS ARE LISTED IN STANDARD ORDER

INTERNUCLEAR DISTANCES FROM GEOMETRY

CENTERS	A.U.	A.
HE - BE	6.400000	3.386688

NUCLEAR REPULSION ENERGY = 1.26000000 A.U.

TAPE 4 HAS BEEN LABELED HEPNT
PSEUDO END-OF-FILE MARKS USED
TAPE 3 IS LOADED WITH THE NAME HEPLS
PSEUDO END-OF-FILE MARKS USED
TAPE 4 SEARCHED FOR FILE ETA+VL
NEW FILE ASSIGNED ON TAPE 4 WITH TAPE NAME HEPNT
THE NEW DIRECTORY IS ... FILE NUMBER FILE NAME
2 ETA+VL
END
FINISHED WRITING FILE ETA+VL

START 1-ELEC. INTS ... ELAPSED CP TIME IS .240 SECONDS

TABLE 16

Coefficients of basis functions of open shell MO's of $HeBe^+$ at an internuclear separation of 6.4 a.u. For exponents of basis functions see Table 15.

HERBP

OPEN ORBITALS
ITERATION 12

POW	1	2	3	4	5	6	7	8	9	10
1S		-5.0837022								
1	.0001230	-.0000444	.0000082	-.0000020	.0000001	-.3413719	-.0042134	-.0293532	-.0867154	-.4310346
	-.0002255	-.3407990	-.0019017	.0080325	-.0373112	-.0002101	.0000528	-.0000181	-.0001305	.0000306
	-.0000277	.0000101	-.0000081							
2S		-1.0725329								
2	.3939299	.4880793	.2203985	.0553382	.0077003	-.0005038	-.0000021	-.0000125	-.0000434	-.0002343
	-.0000003	-.0031525	.0092840	-.0033367	.0006939	-.0001226	-.0037795	-.0000171	-.0002309	.0004550
	-.0056151	.0085144	-.0000281							
3S		-.6651867	.50000							
3	-.0149610	-.0099869	-.0048976	-.0011308	-.0001632	-.1974747	-.0009140	-.0049659	-.0193447	-.1214829
	-.0001150	-.0593251	.1818575	.8329916	.1063963	-.0009183	.0008896	-.0001583	-.0035893	-.0062700
	-.0026914	.0013158	.0001348							
4S		-.2249675								
4	.0645433	.0238402	.0140283	.0029172	.0004462	-.0003927	.0000019	.0000033	.0000527	-.0006076
	.0000001	-.0000009	.0295963	-.0206213	.0027288	.0451958	.1321101	.0084084	.1662263	.3846940
	.4707523	-.0036389	-.0007844							
5S		-.0434947								
5	.1498965	-.0018422	.0152863	.0016823	.0004004	.0169735	.0002676	.0011735	.0061123	.0477574
	.0000292	.0121189	.9003909	-.9290976	.1446152	-.0183071	1.3059689	-.0047851	-.1190486	-.0758184
	-.7570909	.0054282	.0002188							
6S		-.0254742								
6	-.1875245	-.0394034	-.0286761	-.0053938	-.0008740	.0284235	.0004786	.0020837	.0109586	.0861862
	.0000520	.0213992	1.6894647	-1.7116100	.2668823	.0090503	-.7863562	.0095313	.0653752	.0233952
	.4444489	-.0014738	.0017589							
7S		.2157685								
7	.0463869	-.0357316	-.0063785	-.0023831	-.0002595	.0022866	-.0000011	.0000089	-.0000462	-.0007026
	.0000001	.0002197	-.0111319	.0166147	-.0094084	.0887459	1.1556044	.0073502	.0538688	1.5055214
	92.4106951	.0493729	.0002053							
8S		.7163628								
8	-1.5217339	1.2209905	.0352746	.0586871	.0038870	.1982448	.0002371	.0020221	.0039210	.0031637
	.0000415	.0299849	.0429860	.4420953	-.6421168	.0057204	-.2532996	-.0001474	.0143826	.0818460
	-.0254632	.0456383	-.0005161							
9S		.7964282								
9	.4296145	-.2917759	-.0036106	-.0132434	-.0007930	.9745734	.0009769	.0091302	.0149228	-.0203744
	.0001635	.1362977	-1.2846309	3.4763673	-3.4050970	-.0010566	.1043270	-.0004409	-.0177402	.0084809
	-.0298644	-.0147461	-.0011664							
10S		.9480377								
10	.0913811	-.0714579	-.0082478	-.0034827	-.0003533	.0238395	-.0000064	.0001148	-.0003701	-.0070819
	.0000015	.0024735	-.1720281	.1960867	-.0933930	-.0161173	.0633477	-.0162105	-.6933200	.7602827
	-.2269659	.9064925	-.0244687							

89

76

```
11S          1.1261351
11   -.1072631    .0569053   -.0034255    .0020576    .0000465   -.0262995   -.0000087   -.0001782    .0000148    .0041005
     -.0000032   -.0031391    .1296434   -.1756126    .1047895   -.0268037    .5881522   -.0339627   -1.5784902   2.4169195
     -1.7396834   -.4880714    .0115757

12S          4.2767890
12   -.0290430    .0211570   -.0129047    .0003711   -.0001846    .0346698   -.0000518   -.0000411    .0015195   -.0218903
     -.0006027    .0013093   -.0111868   -.0031589   -.0182252   1.4692884    .2503875   -.0013868   -1.8278091   1.4081209
     -.7682088   -.0360544   -.0175250

13S          4.6608162
13   -.0229436   -.0327821    .0380545   -.0001893    .0005548   -3.5937728    .0047603    .0026504    .1419093   2.1116886
      .0002278   -.1435945    .5088848   -1.7441247   2.9012934    .0165055   -.0089072    .0001311   -.0235250    .0217962
     -.0046896   -.0055543    .0008063

14S          5.0762448
14    .8226698   -1.9626165   1.6115087   -.0145324    .0222345    .1080469   -.0001248   -.0000585    .0037530   -.0581498
     -.0003058    .0040659   -.1271282    .1684249   -.1324002    .0099354    .0994311    .0001995   -.0101275   -.0094258
     -.0057392    .0071480    .0125046

15S          6.3875422
15   -.0333599    .0397517   -.0241018   -.0001612   -.0002923   -.0066307    .0000034   -.0000171    .0001303   -.0023038
     -.0000001   -.0004905    .0601072   -.0629488    .0264536    .0405823    .0667399    .0011027   -.0995829    .1761176
     -.1941755   -.5391920   1.1421440

16S          19.1048393
16   -.0192136    .0084576   -.0010870   -.0017735    .0000240   -2.7382524    .0015185   -.0881706    .1914156   3.9381615
     -.0012878   -2.4578431    .2320656   -.7959334   1.4271939   -.0062875   -.0070082    .0080574    .0029406   -.0000851
      .0016073   -.0027239    .0004561

17S          19.5083979
17   -.0021125    .0029342   -.0004819    .0003292   -.0000085   -.0200695    .0000105   -.0005687    .0012595   -.0265462
     -.0000083   -.0160347    .0076184   -.0131053    .0141516   1.0795847    .0957866   -1.2672847   -.7585418    .5264356
     -.2883440   -.0172781    .0068582

18S          25.2463479
18   -.3267210    .9338564   -1.6602484   1.5299329   -.0263584   -.0139433   -.0000011   -.0001238    .0001849   -.0104077
     -.0000019   -.0045287    .0461546   -.0517378    .0275138   -.0002104   -.0389346    .0002489   -.0017197    .0089896
     -.0065379   -.0053364    .0022446

19S          69.3613533
19   -.0100669    .0048790   -.0020280    .0006591   -.0000506   -1.3994456    .0423977   -.1759129    2.3089801   -2.6018414
     -.0009122   -7.3868340    .1135936   -.3859710    .6881693    .0003381   -.0031752   -.0001049   -.0009463    .0016273
     -.0001785   -.0014476    .0002640

20S          171.4757631
20    .1128798   -.3162102    .6157758   -1.0377834   1.2638362   -.0037837    .0000076   -.0001205   -.0002395   -.0022981
     -.0000013    .0019443   -.0160453    .0177940   -.0090364   -.0000686    .0136312    .0000022    .0008269   -.0033862
      .0002678    .0017369   -.0006175

21S          260.4248893
21    .0048869   -.0023502    .0009642   -.0003973    .0001752    .6600130   -.1245668    1.9473384   -2.5252190   1.2540489
      .0145769    1.0562416   -.0550367    .1860413   -.3288820   -.0001543    .0015435    .0000424    .0004513   -.0007863
      .0000621    .0007266   -.0001375

22S          1141.7852471
22    .0021762   -.0010327    .0004088   -.0001346    .0000344    .2891901   -1.5695487    1.6858815   -1.2266056   -.5417529
      .0619957    .0422355   -.0245343    .0827727   -.1457402   -.0000678    .0006864    .0000182    .0002006   -.0003506
      .0000279    .0003264   -.0000503
```

```
235        7022.6446330
23    .0307956   -.0003769    .0001461   -.0000475    .0000112    .1050419   -.9767611    .6273857   -.4297146   -.1952803
     1.2527389    .9993478   -.0089675    .0302350   -.0531650   -.0000247    .0002517    .0000066    .0000733   -.0001282
      .0000103    .0001196   -.0000278

                                                  END OFCALCULATION  ...  ELAPSED CP TIME IS    131.833   SECONDS
```

TABLE 17

Coefficients of basis functions of closed shell MO's of $HeBe^+$ at an internuclear separation of 6.4 a.u. Exponents of basis functions are listed in Table 15.

HEHEP

CLOSED ORBITALS
ITERATION 12

ROW	1	2	3	4	5	6	7	8	9	10
1S	-5.1371523	1.00000								
1	.0001364	-.0000301	.0000140	-.0000005	.0000003	-.3392153	-.0042216	-.0224000	.0869288	-.4320810
	-.0005266	-.0416624	-.0020365	.0070025	-.0366965	-.0002336	.0000497	-.0000288	.0000953	.0000483
	-.0100204	.0000083	-.0000082							
2S	-1.0729687	1.00000								
2	-.3934993	-.4881024	-.2204152	-.0553402	-.0077006	.0005418	.0000022	.0000129	.0000446	-.0002398
	.0000003	.0001590	-.0090282	.0031975	-.0007821	.0001334	.0037532	.0000197	.0002688	-.0001175
	.0056965	-.0084945	.0000287							
3S	-.1897196									
3	-.0756086	-.0242444	-.0152853	-.0030781	-.0004803	.0119502	.0000495	.0002819	.0010220	-.0058875
	.0000064	.0034294	-.0904688	.0048084	-.0101800	-.0436165	-.2098935	-.0078806	-.1547695	-.3299462
	-.4716038	.0040184	.0008082							
4S	-.1126944									
4	-.0602052	-.0274975	-.0138583	-.0030886	-.0004516	-.1088001	-.0004232	-.0024619	.0086627	-.0482071
	-.0000559	-.0302601	1.1427181	-.2301092	.1200604	-.0052377	.0210606	-.0010057	.0207304	-.0328901
	-.0854439	.0031789	.0009981							
5S	-.0347222									
5	-.2087247	-.0122554	-.0246254	-.0035119	-.0006891	-.0176869	-.0001409	-.0006870	.0031024	-.0219548
	-.0000165	-.0076243	-.1358703	.2771837	-.0398973	.0225101	-1.5169880	.0057643	.1425539	.0688085
	.0520678	-.0063240	.0004257							
6S	.0264170									
6	-.0966284	-.0270541	-.0155741	-.0032371	.0004897	.0863461	.0008917	.0041669	.0199257	.1471092
	.0001014	.0443060	1.5608367	-2.2368084	.3623093	.0025215	-.2649137	.0008212	.0222999	-.0114304
	.1850556	-.0013500	.0014106							
7S	.2253370									
7	.0433052	-.0359405	-.0066582	-.0024204	-.0002672	.0029180	.0000110	.0000637	.0002265	.0013412
	.0000014	.0007906	.0000241	-.0117075	-.0019390	.0927122	1.1247982	.0076133	.0529571	1.5283571
	-2.3703372	.0504199	.0001589							
8S	.7174535									
8	1.5441753	-1.2356783	-.0353933	-.0593439	-.0039252	-.1449293	-.0001917	-.0015567	-.0032844	-.0056610
	-.0000323	-.0226823	.1234257	-.2205211	.4439601	-.0058698	.2584025	.0001448	.0147304	-.0842792
	.0258286	-.0469648	.0004649							
9S	.8215504									
9	-.3401375	.2209960	.0016353	.0098486	.0005701	-1.0008493	-.0010359	-.0095173	.0160527	-.0154115
	-.0001920	-.1443452	1.2520492	-3.4065179	3.4354911	.0006099	-.0906103	.0005284	.0229082	-.0223630
	.0359849	.0119703	.0011769							
10S	.9508344									
10	-.0943388	.0731481	.0081693	.0035457	.0003552	-.0227549	.0000079	-.0001030	.0003957	-.0071261
	-.0000013	-.0023024	.1731188	-.1947437	.0902024	.0164536	-.0494139	.0156034	.6621485	-.7088937
	.1861506	-.0155442	.0246886							

```
11S          1.1328796
11    .1053429   -.0555190    .0035368   -.0019961   -.0000410    .0289564    .0000122    .0002064    .0000423   -.0040516
      .0000038    .0036510   -.1288146    .1786285   -.1118562    .0279876   -.5860101    .0343338   1.5901680  -2.4270634
     1.7352523    .4706921   -.0110836

12S          4.2828507
12    .0290551   -.0212470    .0130184   -.0003703    .0001862   -.0361398    .0000540    .0000435    .0015832    .0228216
      .0000023   -.0013571    .0109772    .0023595    .0193354   -1.4690809   -.2500656    .0015284   1.8295337  -1.4066707
      .7673046    .0349531    .0175981

13S          4.6746603
13   -.0221066   -.0344583    .0393969   -.0002029    .0005732   -3.5927539    .0047561    .0026282    .1417974   2.1121857
      .0002273   -.1441047    .5069635   -1.7388444   2.8949959    .0171422   -.0087023    .0001363   -.0241971    .0221929
     -.0089148   -.0055360    .0008044

14S          5.0767161
14   -.0226890   1.9629982   -1.6114744    .0145335   -.0222339   -.1110295    .0001287    .0000599    .0038683   -.0599250
      .0000060   -.0042029    .1275181   -.1697866    .1347015   -.0099978   -.0994567   -.0001978    .0102240    .0093618
      .0057787   -.0071711   -.0125148

15S          6.3876958
15    .0334106   -.0397821    .0241283    .0001610    .0002925    .0066345   -.0000034    .0000172   -.0001305   -.0023060
      .0000001    .0004917   -.0601091    .0629511   -.0264558   -.0406599   -.0667554   -.0010954    .0997289   -.1762297
      .1942372    .5391974   -1.1421461

16S         19.1134010
16    .0199013   -.0084462    .0010750    .0017760   -.0000240    2.7373084   -.0015216    .0881711   -.1915823   3.9379141
      .0012677    2.4579966   -.2319481    .7954160   -1.4266714    .0064728    .0070220   -.0082738   -.0030767    .0001856
     -.0016604    .0027167   -.0004585

17S         19.5154176
17   -.0091115    .0029350   -.0004841    .0003291   -.0000085   -.0205378    .0000108   -.0005835    .0012935   -.0272266
     -.0000085   -.0164522    .0076546   -.0132369    .0143964    1.0794927    .0957410   -1.2672804   -.7583063    .5262351
     -.2882108   -.0172697    .0068480

18S         20.2463781
18   -.3287223    .9338567   -1.6602458    1.5299330   -.0263584   -.0139479   -.0000011   -.0001240    .0001856   -.0104138
     -.0000019   -.0045328    .0461577   -.0517404    .0275169   -.0002106   -.0389351    .0002491   -.0017194    .0089893
     -.0005376   -.0053369    .0022460

19S         69.3074992
19   -.0100644    .0048784   -.0020166    .0006590    .0000506   -1.3993834    .0423990   -.1759268   2.3089945   2.6016168
     -.0009122   -3.3806700    .1135766   -.3859294    .6881052    .0003389   -.0031749   -.0001054   -.0009456    .0016264
     -.0001280   -.0014474    .0002659

20S         171.4757735
20    .1126799   -.3162102    .6157757   -1.0377033   1.2638362    .0037837    .0000076   -.0001205    .0002396   -.0022981
     -.0000613    .0010643   -.0160454    .0177941   -.0090364   -.0000686    .0136312    .0000022    .0008269   -.0033862
      .0002678    .0017369   -.0006195

21S         261.4205899
21   -.0048858    .0023501   -.0009642    .0003973   -.0001752   -.6600078    .1245671   -1.9473377   2.5251962   1.2540358
     -.0145769   -1.9502147    .0550314   -.1060363    .3288777    .0001543   -.0015435   -.0000424    .0004512    .0007862
     -.0000620   -.0007265    .0001375

22S         1141.7677883
22    .0021762   -.0010327    .0004058   -.0001346    .0000344    .2891901   -1.5695487   1.6858805   -1.2266043   -.5417525
      .0619957    .8422344   -.0245342    .0827724   -.1457400   -.0000678    .0006884    .0000182    .0002006   -.0003506
      .0000279    .0003264   -.0000563
```

```
235         7022.644936C
23    .0007956    -.0003769     .0001451    -.0000475     .0000112     .1050419    -.9767611     .6273857     .4297146    -.1952803
     1.2527389     .2993677    -.0089675     .0302349    -.0531650    -.0000247     .0002517     .0000066     .0000733    -.0001282
      .0000103     .0001196    -.0000278
```

TABLE 18

Exponents of Gaussian basis functions is basis set used for computations on HeC^{2+}.

*** GAUSSIAN FUNCTION SPECIFICATIONS ***

NUMBER OF PRIMITIVE GAUSSIANS = 30
NUMBER OF BASIS FUNCTIONS = 30

GAUSSIAN	FUNCTION	COMPONENT	CENTER	TYPE	EXPONENT	COEFFICIENT
1	1	1	HE	S	.1297930	1.0000000
2	2	1	HE	S	.3683640	1.0000000
3	3	1	HE	S	.7256310	1.0000000
4	4	1	HE	S	1.8025690	1.0000000
5	5	1	HE	S	4.9518810	1.0000000
6	6	1	HE	S	1663.5710000	1.0000000
7	7	1	HE	S	246.8036000	1.0000000
8	8	1	HE	S	55.4162900	1.0000000
9	9	1	HE	S	15.4166000	1.0000000
10	10	1	CPP	S	307.5390000	1.0000000
11	11	1	CPP	S	9.4896000	1.0000000
12	12	1	CPP	S	84.5149000	1.0000000
13	13	1	CPP	S	1397.5600000	1.0000000
14	14	1	CPP	S	3.5000200	1.0000000
15	15	1	CPP	S	1.9680300	1.0000000
16	16	1	CPP	S	.4061700	1.0000000
17	17	1	CPP	S	26.9117000	1.0000000
18	18	1	CPP	S	.1351200	1.0000000
19	19	1	CPP	S	9470.5200000	1.0000000
20	20	1	HE	Z	.0044000	1.0000000
21	21	1	HE	Z	.0133000	1.0000000
22	22	1	HE	Z	.0427000	1.0000000
23	23	1	HE	Z	.1522000	1.0000000
24	24	1	HE	Z	1.1347000	1.0000000
25	25	1	CPP	Z	25.3655000	1.0000000
26	26	1	CPP	Z	.0910640	1.0000000
27	27	1	CPP	Z	5.7763600	1.0000000
28	28	1	CPP	Z	1.7873000	1.0000000
29	29	1	CPP	Z	.6577100	1.0000000
30	30	1	CPP	Z	.2480500	1.0000000

THE BASIS FUNCTIONS ARE LISTED IN STANDARD ORDER

INTERNUCLEAR DISTANCES FROM GEOMETRY

CENTERS	A.U.	A.
HE - CPP	3.250000	1.719803

NUCLEAR REPULSION ENERGY = 3.69230769 A.U.

TAPE 4 HAS BEEN LABELED CPPPNT
PSEUDO END-OF-FILE MARKS USED
TAPE 3 IS LOADED WITH THE NAME CPPPLS
PSEUDO END-OF-FILE MARKS USED
TAPE 4 SEARCHED FOR FILE ETA+VL
NEW FILE ASSIGNED ON TAPE 4 WITH TAPE NAME CPPPNT
THE NEW DIRECTORY IS ... FILE NUMBER FILE NAME
2 ETA+VL

TABLE 19

THE CALCULATED ENERGIES FOR $HeC^{2+}(^1\Sigma^+)$ and $HeC^+(^2\Pi)$

R*	+E (HeC^{2+})	+E (HeC^+)
1.5	-38.97863	
2.0	-39.21051	-40.04203
2.5	-39.26808	-40.10535
3.1	-39.28328	
3.15	-39.28348	
3.2	-39.28359	
3.25	-39.28363	
3.3	-39.28355	-40.14061
3.4	-39.28335	
3.5	-39.28292	
3.7	-39.28171	
4.0	-39.27950	-40.14789
4.5	-39.27607	-40.14898
4.7		-40.14908
4.8		-40.14910
4.9		-40.14909
5.0		-40.14908
5.5		-40.14890
6.0		-40.14871
7.0		-40.14847
8.0		-40.14835
10.0	-39.26914	
∞	-39.26887	-40.14822

*R is the internuclear separation in atomic units.

+E is the energy in atomic units.

TABLE 20

Exponents of Gaussian basis functions of basis set used in computations on HeC^+.

*** GAUSSIAN FUNCTION SPECIFICATIONS ***

NUMBER OF PRIMITIVE GAUSSIANS = 35
NUMBER OF BASIS FUNCTIONS = 35

GAUSSIAN	FUNCTION	COMPONENT	CENTER	TYPE	EXPONENT	COEFFICIENT
1	1	1	HE	S	.2445280	1.0000000
2	2	1	HE	S	.8730980	1.0000000
3	3	1	HE	S	3.3042410	1.0000000
4	4	1	HE	S	14.6094000	1.0000000
5	5	1	HE	S	96.7297600	1.0000000
6	6	1	CPP	S	5.1477300	1.0000000
7	7	1	CPP	S	42.4974000	1.0000000
8	8	1	CPP	S	146.0970000	1.0000000
9	9	1	CPP	S	634.8820000	1.0000000
10	10	1	CPP	S	1.9665500	1.0000000
11	11	1	CPP	S	.4962400	1.0000000
12	12	1	CPP	S	14.1892000	1.0000000
13	13	1	CPP	S	4232.6100000	1.0000000
14	14	1	CPP	S	.1533100	1.0000000
15	15	1	CPP	Z	1.1429300	1.0000000
16	16	1	CPP	Z	3.9864000	1.0000000
17	17	1	CPP	Z	18.1557000	1.0000000
18	18	1	CPP	Z	.1146000	1.0000000
19	19	1	CPP	Z	.3594500	1.0000000
20	20	1	HE	Z	.5400000	1.0000000
21	21	1	HE	Z	2.7000000	1.0000000
22	22	1	CPP	X	.1146000	1.0000000
23	23	1	CPP	X	18.1557000	1.0000000
24	24	1	CPP	X	3.9864000	1.0000000
25	25	1	CPP	X	1.1429300	1.0000000
26	26	1	CPP	X	.3594500	1.0000000
27	27	1	HE	X	.5400000	1.0000000
28	28	1	HE	X	2.7000000	1.0000000
29	29	1	CPP	Y	.1146000	1.0000000
30	30	1	CPP	Y	18.1557000	1.0000000
31	31	1	CPP	Y	3.9864000	1.0000000
32	32	1	CPP	Y	1.1429300	1.0000000
33	33	1	CPP	Y	.3594500	1.0000000
34	34	1	HE	Y	.5400000	1.0000000
35	35	1	HE	Y	2.7000000	1.0000000

THE BASIS FUNCTIONS ARE NOT IN STANDARD ORDER

INTERNUCLEAR DISTANCES FROM GEOMETRY

CENTERS	A.U.	A.
HE - CPP	4.900000	2.592933

NUCLEAR REPULSION ENERGY = 2.44897959 A.U.

TAPE 4 HAS BEEN LABELED HEPNT
PSEUDO END-OF-FILE MARKS USED
TAPE 3 IS LOADED WITH THE NAME HEPLS
PSEUDO END-OF-FILE MARKS USED
TAPE 4 SEARCHED FOR FILE ETA+VL

TABLE 21

SPECTROSCOPIC CONSTANTS

		$HeC^{2+}(^1\Sigma^+)$	$HeC^{+}(^2\Pi)$
R_e*	(Angstroms)	1.72	2.59
D_e+	(Kcal/mole)	9.3	.55
ω_e'	(cm^{-1})	493	123
$\omega_e x_e$	(cm^{-1})	5.01	12.6
B_e"	(cm^{-1})	1.89	0.84
α_e	(cm^{-1})	0.977	0.10

---

*R_e is the equilibrium internuclear separation.

+D_e is the dissociation energy.

'ω_e is the vibrational constant.

$\omega_e x_e$ is the anharmonic vibrational constant.

"B_e is the rotational constant.

α_e is the nonrigid rotational correction term.

TABLE 22

Coefficients of basis functions in MO's of HeC^{2+} at an internuclear separation of 3.25 a.u. For exponents of basis functions see Table 18.

CPP DIATOM

MOLECULAR ORBITALS
ITERATION 7

ROW	1	2	3	4	5	6	7	8	9	10
1	A1 -12.5933334	1.00000								
1	-.0018726	.0014630	-.0006701	.0002685	-.0000618	-.0000000	.0000009	-.0000028	.0000266	.0193753
	.4290246	.0775360	.0035880	.3579135	.0453887	-.0098639	.2269961	.0033120	.0004484	.0000734
	-.0002280	.0005592	.0001709	-.0001467	.0000532	.0006302	.0004977	.0003027	-.0000285	-.0001007
2	A1 -1.7099290	1.00000								
2	.0149007	.1604612	.1716149	.1239592	.0594968	.0001147	.0009058	.0047682	.0195649	-.0039655
	-.1167557	-.0161756	-.0007246	-.1722870	.1168255	.6623794	-.0513877	.1385019	-.0000987	.0014695
	-.0044149	.0157605	-.0298700	-.0191727	.0006023	-.0084597	.0044061	.0105437	.0343913	.0266818
3	A1 -1.5268194	1.00000								
3	.0939925	.2679087	.3017243	.2041735	.1003658	.0001906	.0014942	.0079543	.0322161	.0027946
	.0003818	.0112220	.0005046	.1272102	-.1033973	-.4567046	.0364964	-.1630637	.0000637	.0009998
	-.0026099	.0103810	-.0542393	-.0200457	.0016086	-.0306295	.0112037	.0312557	.0748438	.0642715
4	A1 -.8015099									
4	-.0983895	-.1476310	-.1203790	-.0793409	-.0376099	-.0000704	-.0005524	-.0029398	-.0119863	-.0003155
	-.0093087	-.0012862	-.0000576	-.0141396	.0089956	.0624018	-.0040946	.0382038	-.0000072	.0000877
	-.0003909	-.0023393	.0097397	-.0081319	.0099609	.0996631	.0628614	.2130696	.4220448	.4469053
5	A1 -.2788716									
5	-1.6462800	.5799640	-.1843555	.0753703	-.0093381	.0000048	.0001708	-.0001211	.0052553	-.0015006
	-.0553001	-.0069065	-.0002992	-.0533619	-.0273736	.7315410	-.0186664	-.1921894	-.0000353	-.0518021
	.2634453	.3874584	.1470383	-.0045058	-.0026321	.9093671	-.0140062	-.0651305	-.0675664	-.2466418
6	A1 -.2049217									
6	.3436926	-1.0071854	.2616899	-.1575327	.0032942	-.0000313	-.0004746	-.0007619	-.0130030	.0010114
	.0492745	.0055920	.0002323	.0145932	.1189581	-.8946258	.0114174	1.0239607	.0000249	-.0169740
	.1585192	-.4230489	.3491053	.0187636	-.0028589	1.1924445	-.0168595	-.0676302	-.1144404	-.2383086
7	A1 -.1660573									
7	1.7846137	-.9457038	.1819965	-.1291254	-.0032859	-.0000334	-.0004290	-.0009952	-.0113104	.0003237
	.0156932	.0017826	.0000741	.0050430	.0347046	-.2570385	.0036684	.0655578	.0000080	.0124738
	.0743606	.8647123	-.2550441	.0229326	.0021983	-1.0863385	.0132853	.0517496	.0864251	.1193850
8	A1 -.1315096									
8	-.0516320	-.0764288	-.0195613	-.0172525	-.0062548	-.0000121	-.0001000	-.0004965	-.0022480	-.0006292
	-.0211988	-.0027319	-.0001200	-.0262114	.0035504	.2828304	-.0090219	-.0527477	-.0000146	-.2410677
	-1.0865896	.8465880	.0473729	.0084642	-.0008252	.4110163	-.0043041	-.0210181	-.0189458	-.1080229
9	A1 -.0830713									
9	.0789763	-.0041426	.0239089	.0037441	.0039199	.0000060	.0000404	.0002674	.0008099	.0004585
	.0164988	.0020722	.0000961	.0173958	.0059039	-.2441922	.0057595	.1053429	.0000107	-1.4852715
	1.6123685	-.6585454	-.0462734	-.0046453	.0003325	-.2453227	.0015725	.0088750	.0040561	.0522091
10	A1 .0944411									
10	-3.4108198	1.0465002	-.0615804	.0810212	.0111940	.0000323	.0003253	.0011792	.0079839	.0000831
	.0222558	.0018676	.0000651	-.0321714	.1742453	-.8159284	-.0008160	3.1274663	.0000038	-.0383122
	.0652270	-.2781720	2.3624337	.0195835	.0035825	1.1788817	.0162447	.0984758	.0449978	.7325833

11	A1	.1155454								
11	2.5821339	-1.0216698	.1885098	-.1174573	-.0003666	-.0000257	-.0003533	-.0007142	-.0095264	-.0016085
	-.0778885	-.0088042	-.0003662	-.0259506	-.1970341	1.6746984	-.0183259	-2.9783416	-.0000395	-.3605868
	.9790727	-1.7274336	.2785354	.0210730	.0011521	-.8775869	.0085934	.0245956	.0775064	.0162919
12	A1	.5554911								
12	-.0434376	-.4532158	.1218054	-.0442481	-.0042873	-.0000137	-.0001416	-.0004914	-.0035464	-.0002086
	-.0037537	-.0006424	-.0000311	-.0155656	.0353292	-.0444281	-.0030192	.5282339	-.0000045	-.0946772
	.2767981	-.2349783	.7863731	-.0058601	-.0075999	-1.0977501	-.0987233	-.0871083	-1.3738552	2.6787681
13	A1	.8395461								
13	3.3275911	-5.2011191	3.1952234	-.5307821	.2635074	.0002255	.0003523	.0129193	-.0086354	-.0014257
	-.0281969	-.0045780	-.0002188	-.1025673	.1925536	.3398348	-.0203899	-1.2598236	-.0000310	-.0697368
	.2067615	-.3237987	-.3393503	-.0132303	.0011783	-.6001719	.0096618	.0301761	.0227694	.1720893
14	A1	1.8428676								
14	.5724505	-.7243081	.5302707	-.1831797	.0355631	.0000097	-.0002188	.0011277	-.0084380	.0056459
	-.0129460	.0076134	.0004932	.6182504	-2.0768532	2.3547524	.0837220	-1.1715079	.0000389	-.0668615
	.1962521	-.5566177	.5425117	-.8844898	-.0023487	.0934443	.0153465	-.1208826	.3264078	-.3202140
15	A1	2.1888276								
15	1.6929869	-1.2475720	.4002391	.0727997	.0135699	.0000306	.0003160	.0011181	.0079700	.0071171
	.0061932	.0125751	.0007548	.8512759	-2.9678477	3.2592380	.1161737	-2.1606345	.0001416	-.0366929
	.1196611	-.2161411	-.5314906	.6605573	.0014513	-.7230759	-.0098610	.0763980	-.2498267	.3434780
16	A1	3.0529639								
16	.3858868	-.6218013	.8880003	-.4618448	.0832907	.0000151	-.0006466	.0024954	-.0238424	.0000640
	.0000052	.0000802	.0000028	.0009430	-.0256588	.1055644	-.0000265	-.3479848	.0000002	.0227741
	-.0695020	.0146860	-.2861481	.0331769	-.0361651	.4980687	-.0401202	-1.6544911	2.5184852	-1.7824324
17	A1	3.6389596								
17	-1.9642426	4.5317440	-5.8476779	3.3582853	-.4047252	.0000560	.0048462	-.0082988	.1652302	-.0003906
	-.0004727	-.0007477	-.0000432	-.0578622	.3665253	-.5807939	-.0064457	.7406314	-.0000078	.0378795
	-.1131752	.1948905	.1272492	-.0702439	-.0038460	.3264831	-.0185855	-.1702015	.2056630	-.2398591
18	A1	11.5563356								
18	.8977655	-2.4919874	4.3388205	-4.9171116	2.8988615	.0011690	-.0046993	.0865787	-.2931118	.0002767
	.3702176	.0231471	.0007447	-.6357302	.4573864	-.1274333	-.0239994	-.1776661	.0000326	-.0130568
	.0386041	-.0685281	-.0531244	.0004761	-.0002659	-.0612807	.1957941	-.2219424	.1770118	-.0605867
19	A1	11.8847119								
19	-.7805944	.9218070	-1.0089258	.9667002	-.4996986	-.0001956	.0007723	-.0144853	.0490836	.0017457
	2.1559999	.1331786	.0042864	-3.7912397	3.1937319	-2.0586989	-.1359315	1.0313535	.0001981	.0255798
	-.0789219	.1858775	.0835683	-.0405030	.0002803	.2141885	-.0954432	.1137970	-.0718488	.0029441
20	A1	12.4670224								
20	.1475944	-.4549074	.6854266	-.7685200	.4285625	.0001628	-.0006852	.0120053	-.0398780	-.0000537
	-.0890379	-.0054254	-.0001735	.1603814	-.1467055	.0990054	.0058775	.0124511	-.0000074	-.0154477
	.0467425	-.0368271	.0944212	.0075022	-.0001045	-.2646535	-1.5122934	1.9282796	-1.4400505	.8202511
21	A1	36.8904407								
21	-.5438378	1.3924311	-2.4619986	3.3888668	-3.7361621	-.0016325	.0423170	-.2242252	2.4543298	.0003862
	-.0073317	-.0006929	-.0000041	-.0111056	.0525032	-.1196380	.0097144	.1818936	.0000058	.0103110
	-.0305108	.0549324	.0283243	-.0034496	.0032854	.0708952	.0076641	-.0213932	.0089289	-.0283493
22	A1	48.8489535								
22	-.2807780	.2282881	-.1397064	.0635263	-.0336828	-.0000037	.0001665	-.0007882	.0144597	-.0036939
	4.0433883	.1945021	.0019353	-2.9434995	1.6036958	-.9337333	-2.4913900	.4449305	-.0012027	.0108440
	-.0335543	.0787207	.0307837	-.0151569	.0007087	.0949319	-.0001666	-.0014846	.0071324	-.0165582

```
 23   A1      58.6044985
 23   .0068166    .0283519   -.0275078    .0428627   -.0291753    .0000033    .0000632   -.0000403    .0112527   -.0000536
      .0034988    .0001771    .0000027   -.0035690    .0019987    .0059020   -.0016931   -.0379539   -.0000007    .0544948
     -.0136854    .0058193   -.0392323   -.0038868  -1.2582805    .0893962   1.0990208   -.7978167    .5307074   -.3005677

 24   A1     130.1850473
 24   .2731739   -.6893935   1.2034624  -1.6809943   2.1636672    .0146375   -.1459820   1.9909376  -2.5852778   -.0001269
     -.0059557    .0016830    .0000375    .0117867   -.0293451    .0618951    .0002677   -.0930654   -.0000065   -.0052567
      .0155324   -.0279539   -.0146764    .0016683    .0019770   -.0360112   -.0054292    .0101413   -.0032212    .0133696

 25   A1     179.1391465
 25   -.1358717    .1082782   -.0633831    .0252929   -.0115447   -.0000120    .0001108   -.0026257    .0059095   -.1796645
     2.6510566   2.3038723    .0408939  -1.4971605    .7686009   -.4495621  -3.3698186    .2161392   -.0010553    .0053049
     -.0164062    .0384338    .0149645   -.0070204   -.0000606    .0461766    .0002583   -.0009218    .0034858   -.0078150

 26   A1     548.9091633
 26   .1245825   -.3120555    .5390823   -.7420992    .9526330    .0684311  -1.5894074   1.7078024  -1.2695701   -.0005140
     -.0032566    .0000833    .0000372    .0054626   -.0134132    .0283083    .0012644   -.0426787   -.0000045   -.0024032
      .0071074   -.0127943   -.0067946    .0007445    .0005655   -.0164306   -.0020224    .0040626   -.0009480    .0057717

 27   A1     680.3860360
 27   -.0654618    .0518996   -.0308211    .0114673   -.0047832   -.0000209    .0006325   -.0011713    .0021960  -1.9346873
     1.2703326   2.4820502    .1272132   -.7022582    .3649964   -.2154034  -1.9255009    .1041296   -.0144310    .0025641
     -.0079283    .0165596    .0072246   -.0033285   -.0000290    .0222674    .0001217   -.0004315    .0016487   -.0037101

 28   A1    3002.9287411
 28   .0290795   -.0229944    .0132095   -.0049082    .0018988   -.0001576    .0000452    .0001963   -.0007074    1.6596602
     -.5473349   -1.1987985  -1.5640586    .3067558   -.1611516    .0955029    .8290166   -.0462658    .0640460   -.0011405
      .0035262   -.0002528   -.0032125    .0014714    .0000125   -.0098968   -.0000529    .0001888   -.0007274    .0016397

 29   A1    3277.8723477
 29   .0463537   -.1157971    .1992170   -.2721109    .3444243    1.2583626   -.9898554    .6442535   -.4520443    .0003205
     -.0013634   -.0004420   -.0002266    .0020992   -.0050292    .0105644    .0007627   -.0159170    .0000085   -.0008954
      .0026482   -.0047674   -.0025400    .0002758    .0001918   -.0061184   -.0007210    .0014637   -.0003039    .0021164

 30   A1    10406.7913377
 30   .0106592   -.0084305    .0048469   -.0018063    .0007066    .0000080   -.0000316    .0000997   -.0002760    .6191039
     -.1978661   -.4213613   -.9748136    .1117134   -.0589269    .0349708    .2956370   -.0169536    1.2544362   -.0004181
      .0012927   -.0030251   -.0011777    .0005384    .0000045   -.0036273   -.0000193    .0000690   -.0002660    .0006001

                                                    END OFCALCULATION  ...  ELAPSED CP TIME IS    126.280  SECONDS
```

TABLE 23

Coefficients of closed MO basis functions for HeC^+ at internuclear separation 4.9 a.u. For exponents see Table 18.

HECP

CLOSED ORBITALS
ITERATION 11

ROW	1	2	3	4	5	6	7	8	9	10
1S	-11.8964326	1.00000								
1	.0008704	-.0000550	.0000167	-.0000039	.0000003	-.4389766	-.1546655	-.0454532	-.0093420	-.1447111
	-.0011494	-.3589437	-.0012200	-.0003512	.0000078	.0000063	.0000022	.0000362	-.0000236	.0000309
	-.0000094	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000
	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000					
2S	-1.1565531	1.00000								
2	.1399605	.1868193	.0828637	.0210311	.0029099	-.1746295	-.0354122	-.0096154	-.0019850	-.0546127
	.6450280	-.0888295	-.0002547	.3914456	-.0018341	-.0003564	-.0000810	-.0070026	-.0008182	.0042762
	.0005553	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000
	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000					
3S	-1.1226138	1.00000								
3	-.3662875	-.4517184	-.2039578	-.0512043	-.0071242	-.0758379	-.0154562	-.0042214	-.0008679	-.0256758
	.2905913	-.0391454	-.0001117	.1615827	.0040291	.0013706	.0002160	.0108367	.0002283	-.0149349
	.0002488	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000
	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000					
4S	-.3461910									
4	-.0714444	-.0413162	-.0195323	-.0045401	-.0006501	-.0010510	-.0002573	-.0000824	-.0000152	-.0013640
	.0093266	-.0008323	-.0000021	-.0028069	-.2780997	-.0832489	-.0135020	-.3940309	-.4786342	.0043974
	.0012223	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000
	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000					
5S	.1507352									
5	.1723939	.0558210	.0287256	.0061366	.0009056	.0073410	.0031395	.0013002	.0002047	.0407400
	-.2374001	.0145926	.0000315	.2071665	-.1692602	-.0879084	-.0106483	1.2896333	-.8681183	.0042494
	-.0059695	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000
	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000					
6S	.2537918									
6	-.1355473	.2048190	.0204172	.0123315	.0010813	-.0557101	-.0224257	-.0091242	-.0014508	-.2833254
	1.7298809	-.1020277	-.0002218	-1.5859141	-.0381331	-.0106176	-.0017169	.1218154	-.0793440	-.0889070
	.0029914	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000
	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000					
7S	.6887985									
7	-1.5332488	1.2098429	.0310769	.0575192	.0037392	.0097793	.0038747	.0015780	.0002503	.0520043
	-.3599948	.0177822	.0000383	.3993699	-.0022885	.0075726	.0003883	-.3346799	.1321896	.1898539
	-.0037246	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000
	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000					
8S	.9685424									
8	.4469639	-.2861425	-.0138072	-.0125471	-.0009579	-.0283944	-.0061144	-.0018498	-.0003527	-.0324696
	.3931167	-.0186867	-.0000476	-.4337370	.0188594	-.0137638	-.0003888	.4335462	-.1984177	1.0276465
	-.0265359	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000
	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000					
9S	1.5647813									
9	.1636940	-.0380167	.0094667	-.0005951	.0001389	-.0090733	-.0012958	-.0002452	-.0000649	.0045974

	.0481819	-.0018113	-.0000071	-.0603747	1.2853126	.0981589	.0355563	.7787341	-1.6809744	.0563858
	-.0069374	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000
	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000					
10S		4.4150077								
10	.0470176	.0885562	-.1144697	.0003997	-.0017866	1.6611928	.1524868	.0098211	.0062935	-3.0002633
	1.9985170	-.0725006	.0004513	-.7582710	.0101071	.0061282	.0003136	.0524771	-.0392750	.0414223
	.0318944	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000
	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000					
11S		5.0266801								
11	-.8306371	1.9636700	-1.6072078	.0145594	-.0221596	-.1341753	-.0118454	-.0007422	-.0004857	.2592900
	-.2421967	.0060155	-.0000345	.1654591	-.0052606	.0031262	-.0000005	-.1173017	.0368055	-.0200342
	-.0374580	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000
	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000					
12S		6.3545607								
12	.0997295	-.1098662	.0652162	.0002541	.0007879	.0706866	.0059306	.0005190	.0002504	-.1526798
	.1738498	-.0007980	.0000201	-.1290128	.0179273	-.0093657	.0000555	.1211508	-.0598057	.5546308
	-1.1438533	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000
	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000					
13S		7.4656081								
13	.0564896	-.0057187	-.0024392	-.0002278	-.0000307	.0095295	.0007762	.0001025	-.0000347	-.0227103
	.0285155	.0004302	.0000033	-.0224822	1.4844437	-1.3706581	-.0233785	.3000475	-.8446450	.0153169
	.0042247	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000
	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000					
14S		21.9473978								
14	-.0424598	.0228087	.0040051	-.0131277	.0002257	-4.0825232	-.1466525	.1054387	.0014090	2.6504460
	-.9438103	2.3654414	.0017969	.3195804	-.0074656	.0022406	.0006328	-.0244294	.0170700	-.0249258
	.0104265	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000
	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000					
15S		26.1930332								
15	-.3307598	.9357324	-1.6608049	1.5299479	-.0263568	-.0526619	-.0013074	.0010293	.0000199	.0498571
	-.0585489	.0255638	.0000176	.0473641	-.0015681	.0000841	-.0000795	-.0467644	.0149820	-.0139676
	.0057951	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000
	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000					
16S		39.0413216								
16	-.0208461	.0039334	-.0002459	-.0000421	-.0000021	-.0057237	.0001636	.0000529	.0000091	.0071091
	-.0085144	.0020116	.0000012	.0073918	-.5726020	.9736951	-1.2244958	-.1061959	.2876007	-.0070748
	.0008229	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000
	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000					
17S		83.7711885								
17	.0212255	-.0148228	.0063697	-.0019181	-.0002794	2.8891711	2.3759648	-.1569293	.0509979	-1.3709563
	.4433803	-3.7357791	-.0002254	-.1505074	.0034445	-.0013826	.0005128	.0114196	-.0078533	.0111002
	-.0039704	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000
	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000					
18S		171.4214753								
18	-.1134038	.3167258	-.6159496	1.0377560	-1.2638422	-.0074382	-.0012148	-.0001940	.0000002	.0095166
	-.0144869	.0046294	-.0000028	.0153085	-.0006835	.0000740	-.0000100	-.0163652	.0054234	-.0044716
	.0015763	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000
	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000					
19S		314.1429775								
19	-.0102033	.0070885	-.0030631	.0011849	-.0004432	-1.4145761	-2.8367219	2.8370512	-.1157509	.6473944

	-.2115631	2.2605905	.0168220	.0724631	-.0015789	.0005695	-.0001583	-.0054662	.0037257	-.0052880
	.0018301	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000
	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000					
205	1347.0874672									
20	-.0045798	.0031520	-.0013105	.0004428	-.0001116	-.6171048	-1.4273961	1.8638174	-1.6175127	.2862339
	-.0947572	.9922932	.0579385	.0325981	-.0007033	.0002485	-.0003651	-.0024556	.0016711	-.0023734
	.0008144	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000
	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000					
215	8123.9882141									
21	.0016907	-.0011618	.0004800	-.0001588	.0000374	.2243661	.5048474	-.7063810	1.0369535	-.1049579
	.0349315	-.3554888	-1.2662695	-.0120354	.0002591	-.0000911	.0000235	.0009865	-.0006166	.0008759
	-.0002999	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000
	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000					
1X	-.1870553									
22	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000
	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000
	0.0000000	.5566158	.0116047	.0689570	.2390332	.3631649	.0046276	.0001876	0.0000000	0.0000000
	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000					
2X	.1445473									
23	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000
	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000
	0.0000000	1.1714102	-.0118548	-.0998772	-.2042682	-.9210650	.0270322	-.0005362	0.0000000	0.0000000
	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000					
3X	.8958639									
24	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000
	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000
	0.0000000	.0940699	-.0018552	-.0076854	-.0539864	-.0073032	-1.0132004	.0277587	0.0000000	0.0000000
	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000					
4X	1.5518123									
25	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000
	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000
	0.0000000	.6930774	.0357025	.1089424	1.2765679	-1.6248724	-.0618230	-.0002337	0.0000000	0.0000000
	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000					
5X	6.3108525									
26	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000
	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000
	0.0000000	.0330679	.0004127	.0210859	-.0103503	-.0192051	-.5238857	1.1395135	0.0000000	0.0000000
	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000					
6X	7.4669790									
27	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000
	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000
	0.0000000	.2747346	-.0235757	-1.3685270	1.4760413	-.8269779	-.0211769	.0214871	0.0000000	0.0000000
	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000					
7X	39.0434659									
28	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000
	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000
	0.0000000	.0939476	1.2242857	-.9725256	.5686611	-.2786302	-.0042927	.0015812	0.0000000	0.0000000
	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000					
1 Y	-.1870553									
29	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000

	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000
	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	.5560158	.0116047
	.0689570	.2390332	.3631649	.0046276	.0001876					
2 Y	.1445473									
30	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000
	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000
	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	1.1714102	-.0118548
	-.0998772	-.2042682	-.9210650	.0270322	-.0005362					
3 Y	.8958639									
31	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000
	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000
	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	.0940099	-.0018552
	-.0876854	-.0539864	-.0073032	-1.0132004	.0277587					
4 Y	1.5518123									
32	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000
	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000
	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	.6930774	.0357025
	.1005424	1.2765679	-1.6248724	-.0618230	-.0002337					
5 Y	6.3108525									
33	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000
	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000
	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	.0330679	.0004127
	.0216859	-.0103503	-.0192051	-.5238857	1.1395135					
6 Y	7.4669790									
34	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000
	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000
	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	.2747346	-.0235757
	-1.3685276	1.4760413	-.8209779	-.0211769	.0214871					
7 Y	39.0434659									
35	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000
	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000
	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	.8939476	1.2242857
	-.9725256	.5686611	-.2786302	-.0042927	.0015812					

TABLE 24

Coefficients of basis functions in open MO's for HeC^+ at internuclear separation 4.9 a.u. For exponents see Table 20.

HECP

OPEN ORBITALS
ITERATION 11

ROH	1	2	3	4	5	6	7	8	9	10
1S	-10.4635898									
1	-.0001316	.0005284	-.0000358	.0000004	-.0000009	.4375641	.1544176	.0453907	.0093286	.1455725
	.0042295	.3583511	-.0012184	.0017723	-.0000112	-.0000103	-.0000027	-.0000446	.0000321	-.0000365
	.0000114	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000
	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000					
2S	-.9010944									
2	-.0570543	-.0527060	-.0242652	-.0058891	-.0008315	-.0004446	-.0000944	-.0000282	-.0000054	-.0003370
	.0037319	-.0002785	-.0000067	-.0020500	-.3717162	-.1085195	-.0172527	-.1556001	-.5590245	.0018833
	.0003442	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000
	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000					
3S	-.7934680									
3	.3903009	.4860658	.2192395	.0550848	.0076618	-.0031299	-.0005961	-.0001469	-.0000325	.0001688
	.0053291	-.0012600	-.0000048	.0110810	-.0236909	-.0069315	-.0011191	-.0178291	-.0367188	.0106494
	-.0000282	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000
	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000					
4S	-.2501412									
4	.0212980	-.0508925	-.0098395	-.0038360	-.0004137	-.1203618	-.0225396	-.0053701	-.0012202	.0266346
	-.1121955	-.0443560	-.0001476	1.0755785	-.0232548	-.0101899	-.0011934	.1720531	-.0860330	.0191563
	-.0039825	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000
	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000					
5S	-.1999516									
5	.1842715	.0515711	.0307370	.0062726	.0009587	.0582124	.0132598	.0040109	.0007695	.0538349
	-.4475528	.0394694	.0001036	.1643115	-.2068490	-.0762250	-.0058126	1.2409355	-.5892130	.0118577
	-.0056979	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000
	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000					
6S	-.1474557									
6	.0262535	-.1201081	-.0177839	-.0080184	-.0007910	.1631747	.0393533	.0125915	.0023246	.2182234
	-1.8109037	.1281131	.0003208	1.2665227	.0668490	.0195629	.0028859	-.2974092	.1283073	.0503297
	-.0010413	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000
	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000					
7S	.4894948									
7	1.5670892	-1.2390323	-.0342957	-.0590745	-.0038893	-.0201752	-.0043052	-.0013166	-.0002490	-.0219947
	.2895979	-.0133901	-.0000338	-.3414779	-.0124560	-.0091654	-.0007852	.3437923	-.1100823	-.0303455
	-.0022094	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000
	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000					
8S	.7467527									
8	.2982871	-.1743593	-.0139360	-.0073152	-.0006705	-.0384470	-.0061559	-.0014222	-.0003255	.0057842
	.2757866	-.0123681	-.0000390	-.3225323	-.0351139	-.0161797	-.0015578	.3457352	-.1025204	1.0404339
	-.0277132	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000
	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000					
9S	1.0122471									
9	.2131763	-.0592970	.0100565	-.0013270	.0001130	-.0127295	-.0017775	-.0003334	-.0000888	.0077487

	.0617192	-.0024398	-.0000097	-.0782428	1.2247775	.3107565	.0337295	.8998156	-1.7642670	.0965922
	-.0083321	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000
	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000					
10S	3.7310288									
10	-.0848653	-.0181192	.0612764	.0003525	.0009813	-1.6474828	-.1510837	-.0101882	-.0062609	3.0036442
	-2.0465903	.0645903	-.0004560	.8092730	-.0105978	-.0063843	-.0003373	-.0624329	.0438080	-.0523738
	-.0237600	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000
	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000					
11S	4.8272062									
11	.8302302	-1.9666318	1.6100988	-.0145875	.0221997	.0785645	.0067533	.0004625	.0002783	-.1606206
	.1776378	-.0028332	.0000204	-.1417739	.0064752	-.0042573	-.0000154	.1169430	-.0371130	.0212104
	.0348710	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000
	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000					
12S	6.1514925									
12	-.0933664	.1035586	-.0632750	-.0008351	-.0007627	-.0558568	-.0046088	-.0004873	-.0001991	.1273308
	-.1562655	-.0007051	-.0000172	.1215087	-.0253579	.0158637	.0000685	-.1210329	.0635969	-.5536828
	1.1440247	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000
	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000					
13S	6.7261653									
13	.0586030	-.0045304	-.0036778	-.0002245	-.0000467	.0095156	.0007753	.0001044	.0000348	-.0228552
	.0289366	.0004667	.0000033	-.0229160	1.5071861	-1.3669424	-.0245381	.3217737	-.8733394	.0136440
	.0095486	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000
	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000					
14S	21.1312033									
14	.0436901	-.0246324	-.0017135	.0112826	-.0001892	4.0875065	.1460189	-.1052543	-.0014266	-2.6616520
	.9529041	-2.3648533	-.0017942	-.3238811	.0075538	-.0022575	-.0006394	.0248895	-.0173383	.0254080
	-.0107283	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000
	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000					
15S	25.9937299									
15	.3307974	-.9358070	1.6608498	-1.5299642	.0263568	.0476926	.0010893	-.0008980	-.0000194	-.0466106
	.0493799	-.0226626	-.0000155	-.0469167	.0015753	-.0000903	.0000840	.0467943	-.0149963	.0141510
	-.0060731	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000
	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000					
16S	38.1942982									
16	-.0210662	.0039771	-.0002478	-.0000459	-.0000021	-.0057535	.0001646	.0000531	.0000091	.0071532
	-.0005803	.0020203	.0000012	.0074556	-.5754165	.9757047	-1.2244752	-.1072156	.2897987	-.0071547
	.0003356	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000
	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000					
17S	82.9065710									
17	-.0213273	.0149066	-.0064174	.0019405	.0002753	-2.8914152	-2.3759601	.1568937	-.0509898	1.3729950
	-.4444973	3.7367931	.0002201	.1510808	-.0034550	.0013858	-.0005137	-.0114673	.0078828	-.0111492
	.0039899	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000
	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000					
18S	171.2220131									
18	-.1134076	.3167307	-.6159520	1.0377569	-1.2638422	-.0074216	-.0012038	-.0001973	.0000605	.0095052
	-.0144748	.0040127	-.0000029	.0153060	-.0006839	.0000741	-.0000101	-.0163671	.0054244	-.0044784
	.0015842	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000
	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000					
19S	313.2634357									
19	.0102161	-.0070986	.0030684	-.0011877	.0004450	1.4148978	2.8368185	-2.8370573	.1157497	-.6476574

	.2117161	-2.2608236	-.0168218	-.0725370	.0015801	-.0005699	.0001584	.0054722	-.0037294	.0052941
	-.0818323	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000
	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000					
2S	1346.2041370									
20	-.0045811	.0031530	-.0013109	.0004430	-.0001117	-.6171374	-1.4274093	1.8638221	-1.6175130	.2862608
	-.0947731	.9923176	.0579385	.0326058	-.0007034	.0002485	-.0000651	-.0024562	.0016715	-.0023748
	.0008146	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000
	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000					
2IS	8123.1040971									
21	-.0016908	.0011619	-.0004800	.0001588	-.0000374	-.2243680	-.5048482	.7063813	-1.0369536	.1049595
	-.0349325	.3554903	1.2662695	.0120359	-.0002591	.0000911	-.0000235	-.0009065	.0006167	-.0008759
	.0002999	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000
	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000					
1X	-.9025186	.25000								
22	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000
	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000
	0.0000000	.1574697	.0172374	.1684310	.3712393	.5589231	.0001658	.0001313	0.0000000	0.0000000
	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000					
2X	-.2218764									
23	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000
	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000
	0.0000000	-1.2326592	.0100487	.0779736	.2112065	.6002591	-.0162895	-.0000891	0.0000000	0.0000000
	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000					
3X	.6971301									
24	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000
	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000
	0.0000000	-.0231635	.0038361	.0135256	.1296704	-.1224459	1.0071363	-.0274266	0.0000000	0.0000000
	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000					
4X	.9931602									
25	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000
	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000
	0.0000000	.7864600	.0335366	.1111343	1.2115633	-1.6992306	-.1277516	.0020176	0.0000000	0.0000000
	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000					
5X	6.1122009									
26	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000
	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000
	0.0000000	-.0277909	-.0007981	-.0431295	.0354831	.0042748	.5236615	-1.1390224	0.0000000	0.0000000
	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000					
6X	6.7116618									
27	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000
	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000
	0.0000000	.2878360	-.0244876	-1.3646591	1.4963690	-.8477316	-.0303760	.0399387	0.0000000	0.0000000
	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000					
7X	38.1837983									
28	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000
	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000
	0.0000000	-.0948356	-1.2242740	.9741789	-.5711886	.2806614	.0043414	-.0016036	0.0000000	0.0000000
	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000					
1 Y	-.9025186	.25000								
29	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000

```
        0.0000000   0.0000000   0.0000000   0.0000000   0.0000000   0.0000000   0.0000000   0.0000000   0.0000000   0.0000000
        0.0000000   0.0000000   0.0000000   0.0000000   0.0000000   0.0000000   0.0000000   0.0000000    .1574697    .0172374
         .1084310    .3712393    .5589231    .0001608    .0001313

 2 Y          -.2218764
30   0.0000000   0.0000000   0.0000000   0.0000000   0.0000000   0.0000000   0.0000000   0.0000000   0.0000000   0.0000000
        0.0000000   0.0000000   0.0000000   0.0000000   0.0000000   0.0000000   0.0000000   0.0000000   0.0000000   0.0000000
        0.0000000   0.0000000   0.0000000   0.0000000   0.0000000   0.0000000   0.0000000   0.0000000  -1.2326592    .0100487
         .0779736    .2112665    .6002591   -.0162895   -.0000891

 3 Y           .6971301
31   0.0000000   0.0000000   0.0000000   0.0000000   0.0000000   0.0000000   0.0000000   0.0000000   0.0000000   0.0000000
        0.0000000   0.0000000   0.0000000   0.0000000   0.0000000   0.0000000   0.0000000   0.0000000   0.0000000   0.0000000
        0.0000000   0.0000000   0.0000000   0.0000000   0.0000000   0.0000000   0.0000000   0.0000000   -.0231635    .0038361
         .0135256    .1296704   -.1224459   1.0071363   -.0274266

 4 Y           .9931662
32   0.0000000   0.0000000   0.0000000   0.0000000   0.0000000   0.0000000   0.0000000   0.0000000   0.0000000   0.0000000
        0.0000000   0.0000000   0.0000000   0.0000000   0.0000000   0.0000000   0.0000000   0.0000000   0.0000000   0.0000000
        0.0000000   0.0000000   0.0000000   0.0000000   0.0000000   0.0000000   0.0000000   0.0000000    .7864600    .0335366
         .1111343   1.2115633  -1.6992306   -.1277516    .0020176

 5 Y          6.1122009
33   0.0000000   0.0000000   0.0000000   0.0000000   0.0000000   0.0000000   0.0000000   0.0000000   0.0000000   0.0000000
        0.0000000   0.0000000   0.0000000   0.0000000   0.0000000   0.0000000   0.0000000   0.0000000   0.0000000   0.0000000
        0.0000000   0.0000000   0.0000000   0.0000000   0.0000000   0.0000000   0.0000000   0.0000000   -.0277909   -.0007901
        -.0431295    .0354831    .0042748    .5236615  -1.1390224

 6 Y          6.7116618
34   0.0000000   0.0000000   0.0000000   0.0000000   0.0000000   0.0000000   0.0000000   0.0000000   0.0000000   0.0000000
        0.0000000   0.0000000   0.0000000   0.0000000   0.0000000   0.0000000   0.0000000   0.0000000   0.0000000   0.0000000
        0.0000000   0.0000000   0.0000000   0.0000000   0.0000000   0.0000000   0.0000000   0.0000000    .2878980   -.0244876
       -1.3648591   1.4963690   -.8477316   -.0303760    .0399387

 7 Y         38.1837983
35   0.0000000   0.0000000   0.0000000   0.0000000   0.0000000   0.0000000   0.0000000   0.0000000   0.0000000   0.0000000
        0.0000000   0.0000000   0.0000000   0.0000000   0.0000000   0.0000000   0.0000000   0.0000000   0.0000000   0.0000000
        0.0000000   0.0000000   0.0000000   0.0000000   0.0000000   0.0000000   0.0000000   0.0000000   -.0948356  -1.2242748
         .9741789   -.5711886    .2806614    .0043414   -.0016038

                                                END OFCALCULATION  ...  ELAPSED CP TIME IS    231.318   SECONDS
```

TABLE 25

Orbital exponents used in calculations on He_3^{2+}.

GAUSSIAN FUNCTION SPECIFICATIONS

NUMBER OF PRIMITIVE GAUSSIANS = 12
NUMBER OF BASIS FUNCTIONS = 12

GAUSSIAN	FUNCTION	COMPONENT	CENTER	TYPE	EXPONENT	COEFFICIENT
1	1	1	HEPP1	S	.2980730	1.0000000
2	2	1	HEPP1	S	1.2425670	1.0000000
3	3	1	HEPP1	S	5.7829400	1.0000000
4	4	1	HEPP1	S	38.4749000	1.0000000
5	5	1	HEPP2	S	.2980730	1.0000000
6	6	1	HEPP2	S	1.2425670	1.0000000
7	7	1	HEPP2	S	5.7829400	1.0000000
8	8	1	HEPP2	S	38.4749000	1.0000000
9	9	1	HEPP3	S	.2980730	1.0000000
10	10	1	HEPP3	S	1.2425670	1.0000000
11	11	1	HEPP3	S	5.7829400	1.0000000
12	12	1	HEPP3	S	38.4749000	1.0000000

THE BASIS FUNCTIONS ARE LISTED IN STANDARD ORDER

INTERNUCLEAR DISTANCES FROM GEOMETRY

CENTERS	A.U.	A.
HEPP1 - HEPP2	1.920000	1.016006
HEPP1 - HEPP3	1.920000	1.016006
HEPP2 - HEPP3	3.840000	2.032013

NUCLEAR REPULSION ENERGY = 5.20833333 A.U.

PSEUDO END-OF-FILE MARKS USED

TABLE 26

ENERGIES AT VARIOUS INTERNUCLEAR SEPARATIONS OF He_3^{2+}

R_1	R_2	E
1.34	0.67	-3.55334
1.54	0.66	-5.61162
1.14	0.64	-5.36692
1.34	0.57	-5.02180
1.34	0.76	-5.85577
1.34	1.34	-6.46595
1.34	1.24	-6.43502
1.34	1.44	-6.48521
2.12	2.12	-6.46113
1.92	1.92	-6.49157
2.02	2.12	-6.46889
2.02	2.02	-6.47662
1.92	2.02	-6.48429
1.72	1.72	-6.51481
1.52	1.52	-6.51482
1.42	1.42	-6.49618

TABLE 27

ENERGIES OF $HeBe^{2+}$ AT SHORT INTERNUCLEAR DISTANCES

R (a)	E (b)
0.3	-2.31068
0.4	-7.34585
0.6	-11.95852
0.75	-13.66424
0.9	-14.70426
1.0	-15.17226
1.5	-16.21595

(a) R is internuclear distance in atomic units.

(b) E is energy in atomic units.

TABLE 28

Orbital exponents used in calculations on $HeBe^{2+}$ (see Section V of text).

*** GAUSSIAN FUNCTION SPECIFICATIONS ***

NUMBER OF PRIMITIVE GAUSSIANS = 30
NUMBER OF BASIS FUNCTIONS = 30

GAUSSIAN	FUNCTION	COMPONENT	CENTER	TYPE	EXPONENT	COEFFICIENT
1	1	1	BEPP	S	1.3543100	1.0000000
2	2	1	BEPP	S	.1502300	1.0000000
3	3	1	BEPP	S	32.6562000	1.0000000
4	4	1	BEPP	S	117.7990000	1.0000000
5	5	1	BEPP	S	532.2800000	1.0000000
6	6	1	BEPP	S	3.6682600	1.0000000
7	7	1	BEPP	S	3630.3800000	1.0000000
8	8	1	BEPP	S	.0524060	1.0000000
9	9	1	BEPP	S	10.4801000	1.0000000
10	10	1	BEPP	S	.3890500	1.0000000
11	11	1	HE	S	.1297930	1.0000000
12	12	1	HE	S	.3683640	1.0000000
13	13	1	HE	S	.7256310	1.0000000
14	14	1	HE	S	1.8025690	1.0000000
15	15	1	HE	S	4.9518810	1.0000000
16	16	1	HE	S	1663.5710000	1.0000000
17	17	1	HE	S	246.8036000	1.0000000
18	18	1	HE	S	55.4102900	1.0000000
19	19	1	HE	S	15.4166000	1.0000000
20	20	1	HE	Z	.0044000	1.0000000
21	21	1	HE	Z	.0133000	1.0000000
22	22	1	HE	Z	.0427000	1.0000000
23	23	1	HE	Z	.1522000	1.0000000
24	24	1	HE	Z	1.1347000	1.0000000
25	25	1	BEPP	Z	8.3500000	1.0000000
26	26	1	BEPP	Z	1.9600000	1.0000000
27	27	1	BEPP	Z	.5700000	1.0000000
28	28	1	BEPP	Z	.2120000	1.0000000
29	29	1	BEPP	Z	.0820000	1.0000000
30	30	1	BEPP	Z	.0330000	1.0000000

THE BASIS FUNCTIONS ARE LISTED IN STANDARD ORDER

INTERNUCLEAR DISTANCES FROM GEOMETRY

CENTERS	A.U.	A.
BEPP - HE	.200000	.105834

NUCLEAR REPULSION ENERGY = 40.00000000 A.U.

PSEUDO END-OF-FILE MARKS USED
PSEUDO END-OF-FILE MARKS USED

START 1-ELEC. INTS ... ELAPSED CP TIME IS .281 SECONDS

TABLE 29

V(r) VALUES IN eV CALCULATED FROM MO-SCF AND FROM BORN-MAYER FITS OF EXPERIMENTAL AND THEORETICAL DATA

R(Å)	V(r)$_{MO}$ [a]	V(r) Eq.12 [b]	V(r) Expt. [c]
0.1588	385.4	351.0	242.8
0.2116	248.4	252.5	179.6
0.3174	122.8	130.6	98.3
0.3967	76.4	79.7	62.5
0.4761	48.1	48.6	39.8
0.5292	35.4	35.0	29.4
0.7935	7.0	6.7	6.5

(a) Based directly on MO-SCF calculations.

(b) From least squares fit of V(r)$_{MO}$ to Born-Mayer potential (Eq.12).

(c) From interaction potential given in Reference 75 and Eq.13.

TABLE 30

$HeBe^{+2}$ UNITED ATOM AND SEPARATED ATOM AND ION ENERGIES IN ATOMIC UNITS

C^{+2} united ion		He atom	Be^{+2} ion
This calculation	-36.4070	-2.8617	-13.6109
Best SCF	-36.4085 (a)	-2.8617 (a)	-13.6113 (a)
Experimental	-36.5466 (b)	-2.9034 (b)	-13.6561 (b)

(a) See Reference 89.

(b) C. Moore, National Bureau of Standards (U.S.), Circular 467 (1949).

TABLE 31

ORBITAL ENERGIES FOR $HeBe^{2+}$ AT SHORT INTERNUCLEAR SEPARATIONS

R (a)	E_1 (b)	E_2 (c)
0.0	-12.6406	-1.6919
0.2	-10.6862	-1.5744
0.3	- 9.2399	-1.4667
0.6	- 6.9526	-1.8464
0.75	- 6.3920	-2.007
0.9	- 6.0610	-2.1023
1.0	- 5.9202	-2.1312

(a) R in atomic units.

(b) E_1 is first orbital energy in atomic units.

(c) E_2 is second orbital energy in atomic units.

TABLE 32

Orbital exponents of expanded basis set used in calculations on $HeBe^{2+}$ (see Section VI of text).

GAUSSIAN FUNCTION SPECIFICATIONS

NUMBER OF PRIMITIVE GAUSSIANS = 32
NUMBER OF BASIS FUNCTIONS = 32

GAUSSIAN	FUNCTION	COMPONENT	CENTER	TYPE	EXPONENT	COEFFICIENT
1	1	1	BEPP	S	1.3543100	1.0000000
2	2	1	BEPP	S	.1502300	1.0000000
3	3	1	BEPP	S	32.6562000	1.0000000
4	4	1	BEPP	S	117.7990000	1.0000000
5	5	1	BEPP	S	532.2300000	1.0000000
6	6	1	BEPP	S	3.6682600	1.0000000
7	7	1	BEPP	S	3630.3200000	1.0000000
8	8	1	BEPP	S	.0524860	1.0000000
9	9	1	BEPP	S	10.4801000	1.0000000
10	10	1	BEPP	S	.3890500	1.0000000
11	11	1	HE	S	.1297930	1.0000000
12	12	1	HE	S	.3033640	1.0000000
13	13	1	HE	S	.7256310	1.0000000
14	14	1	HE	S	1.8025690	1.0000000
15	15	1	HE	S	4.9518810	1.0000000
16	16	1	HE	S	1663.5710000	1.0000000
17	17	1	HE	S	246.8036000	1.0000000
18	18	1	HE	S	55.4102900	1.0000000
19	19	1	HE	S	15.4166000	1.0000000
20	20	1	HE	Z	.0944000	1.0000000
21	21	1	HE	Z	-.0085000	1.0000000
22	22	1	HE	Z	.0133000	1.0000000
23	23	1	HE	Z	.0427000	1.0000000
24	24	1	HE	Z	.1522000	1.0000000
25	25	1	HE	Z	1.1347000	1.0000000
26	26	1	HE	Z	-.8256000	1.0000000
27	27	1	BEPP	Z	8.3500000	1.0000000
28	28	1	BEPP	Z	1.9600000	1.0000000
29	29	1	BEPP	Z	.5700000	1.0000000
30	30	1	BEPP	Z	.2120000	1.0000000
31	31	1	BEPP	Z	.0820000	1.0000000
32	32	1	BEPP	Z	.0330000	1.0000000

THE BASIS FUNCTIONS ARE LISTED IN STANDARD ORDER

INTERNUCLEAR DISTANCES FROM GEOMETRY

CENTERS	A.U.	A.
BEPP - HE	.300000	.158751

NUCLEAR REPULSION ENERGY = 26.66666667 A.U.

PSEUDO END-OF-FILE MARKS USED
PSEUDO END-OF-FILE MARKS USED

START 1-ELEC. INTS ... ELAPSED CP TIME IS .281 SECONDS

FIGURE 1

GEOMETRY AND SYMMETRY GROUPS FOR THE

CALCULATED H_n^+ CLUSTERS

The parameters a, b, c are distances from the center of an H_2 to the center of H_3^+. The open and closed circles represent the centers of mass for H_2 molecules whose axes are orthogonal to the lines a or c or along the lines b, respectively.

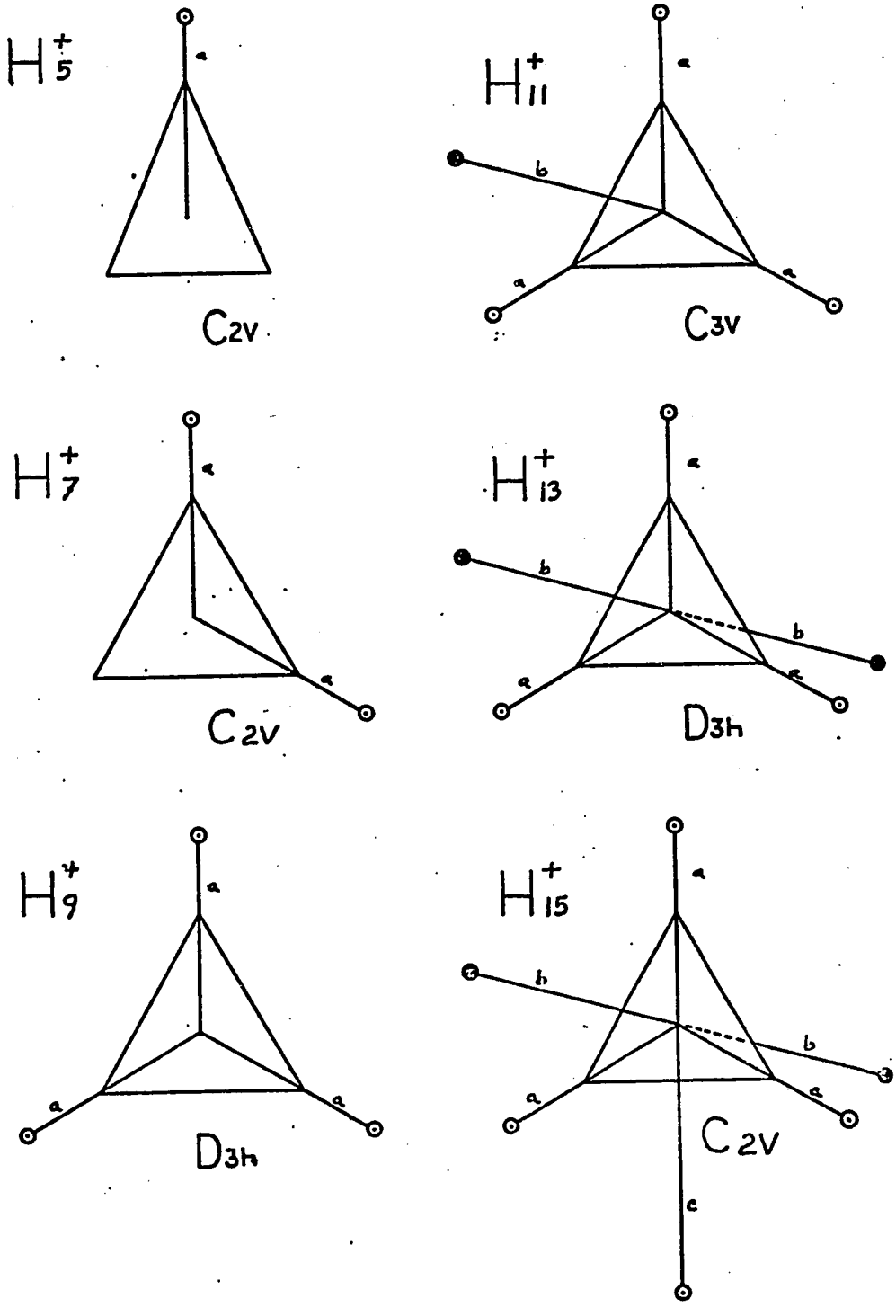

H_5^+
a
C_{2V}
H_{11}^+
a
b
a
a
C_{3V}
H_7^+
a
a
C_{2V}
H_{13}^+
a
b
b
a
a
D_{3h}
H_9^+
a
a
a
D_{3h}
H_{15}^+
a
b
b
a
a
C_{2V}
c

FIGURE 2

PLOT OF ENERGY AGAINST DISTANCE

FOR H_{11}^{+} (SEE TEXT FOR GEOMETRY)

E is energy in atomic units; R is distance between center of H_3^+ triangle and center of any H_2 pair (in atomic units).

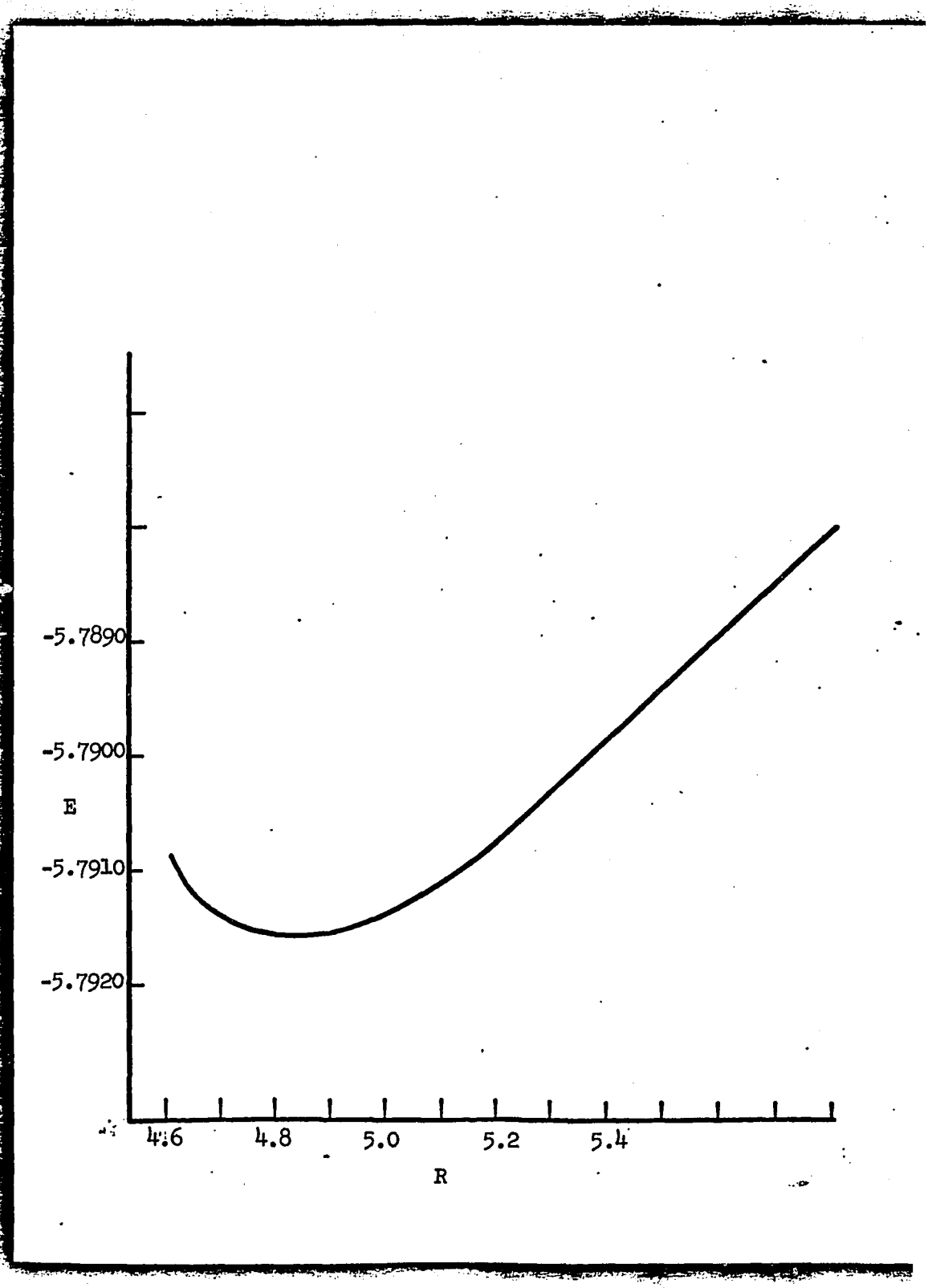

-5.7890
-5.7900
E
-5.7910
-5.7920
4.6
4.8
5.0
5.2
5.4
R

FIGURE 3

ENERGY VERSUS DISTANCE FOR H_{11}^{+}

E is energy in atomic units;

R is distance from center of H^{+}_{3} triangle to center of any H_2 pair (in atomic units).

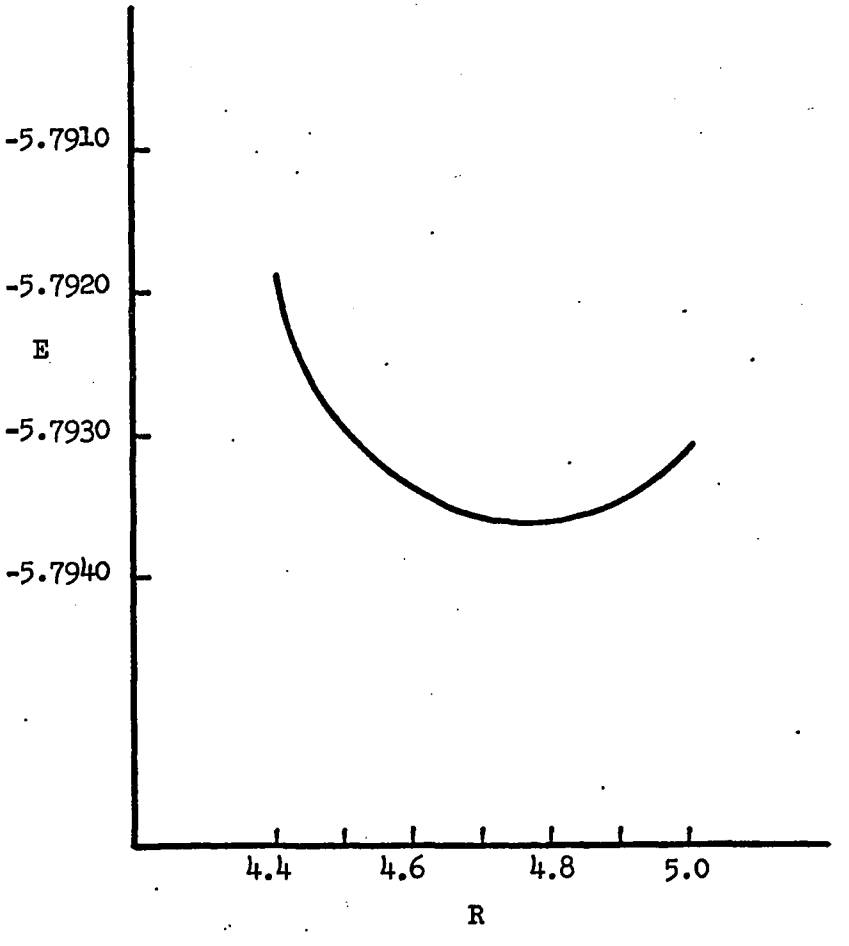

-5.7910
-5.7920
E
-5.7930
-5.7940
4.4
4.6
4.8
5.0
R

FIGURE 4

ENERGY VERSUS DISTANCE FOR

$Be^{2+}He$

E is energy in atomic units;

R is internuclear distance in atomic units.

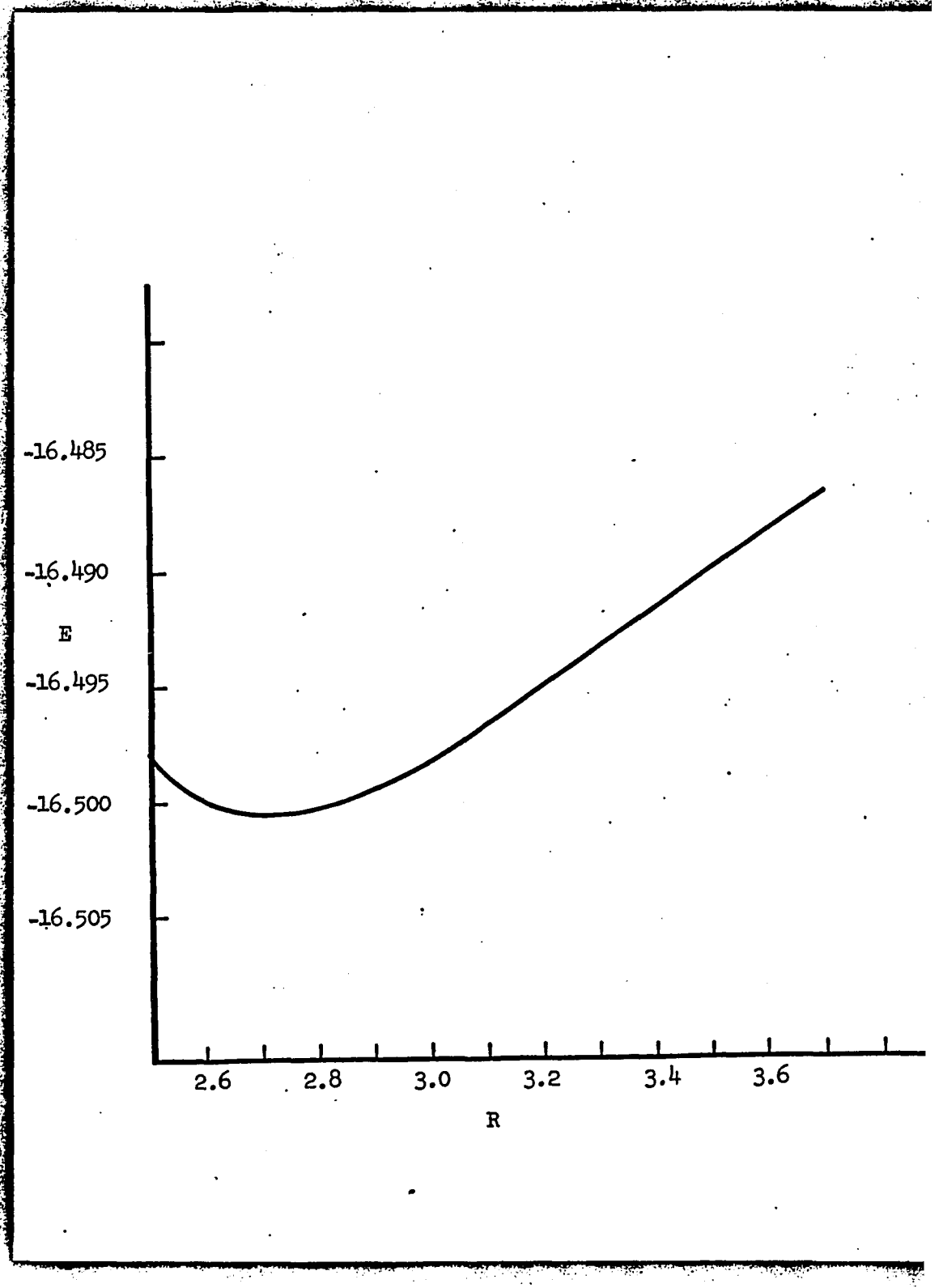

-16.485
-16.490
E
-16.495
-16.500
-16.505
2.6
2.8
3.0
3.2
3.4
3.6
R

FIGURE 5

ENERGY VERSUS DISTANCE FOR Be^{2+} $(He)_2$

E is energy in atomic units;

R is internuclear distance (Be-He)
in atomic units.

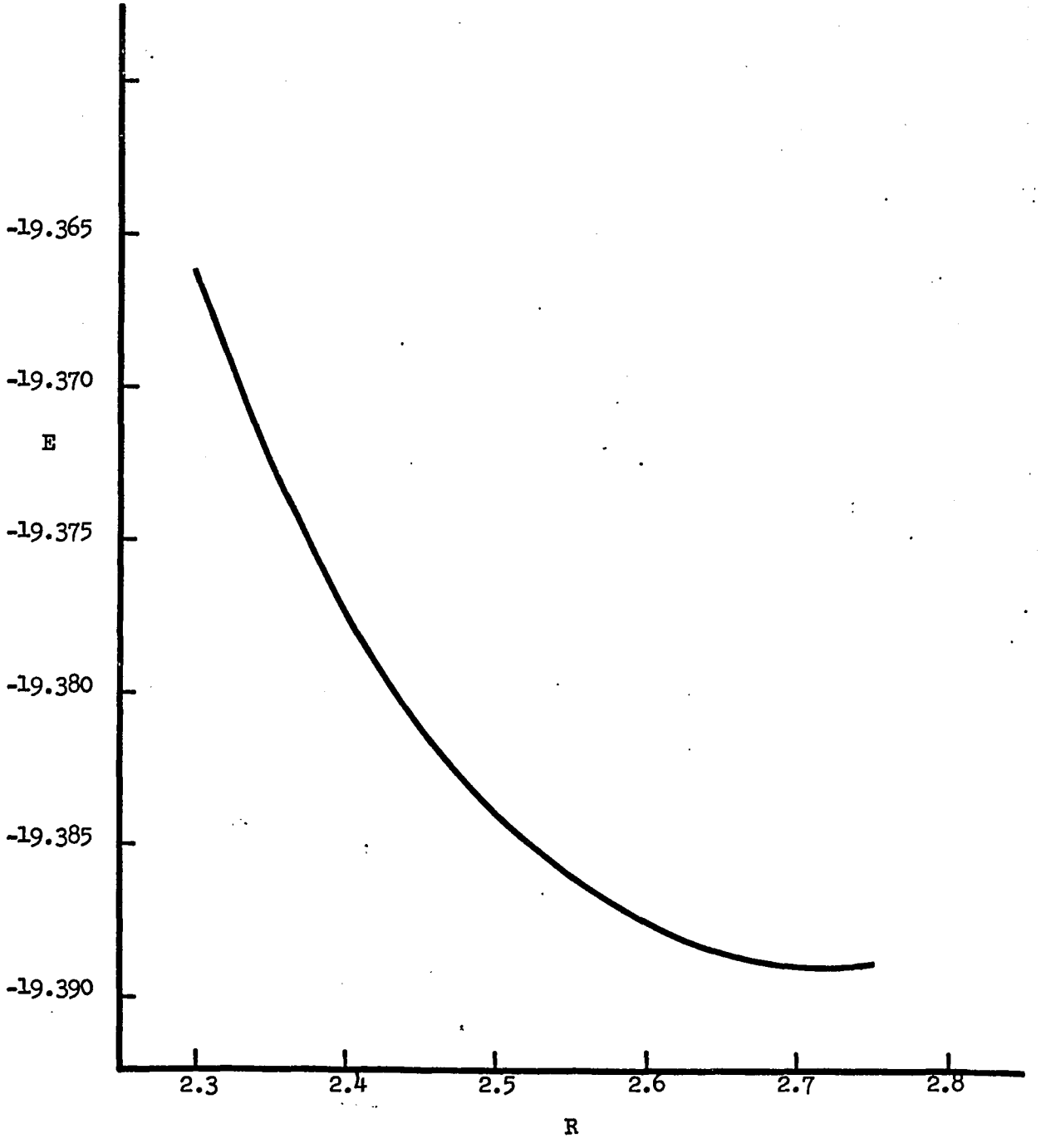

-19.365
-19.370
E
-19.375
-19.380
-19.385
-19.390
2.3
2.4
2.5
2.6
2.7
2.8
R

FIGURE 6

ENERGY CURVES FOR THE MOLECULAR IONS HeC^{2+} AND HeC^{+}

E is for the energy in kcal/mole relative to the asymptomic limits C^{2+}, He and C^{+}, He. R is the distance in atomic units.

Curve A is for HeC^{2+}, and
Curve B is for HeC^{+}.

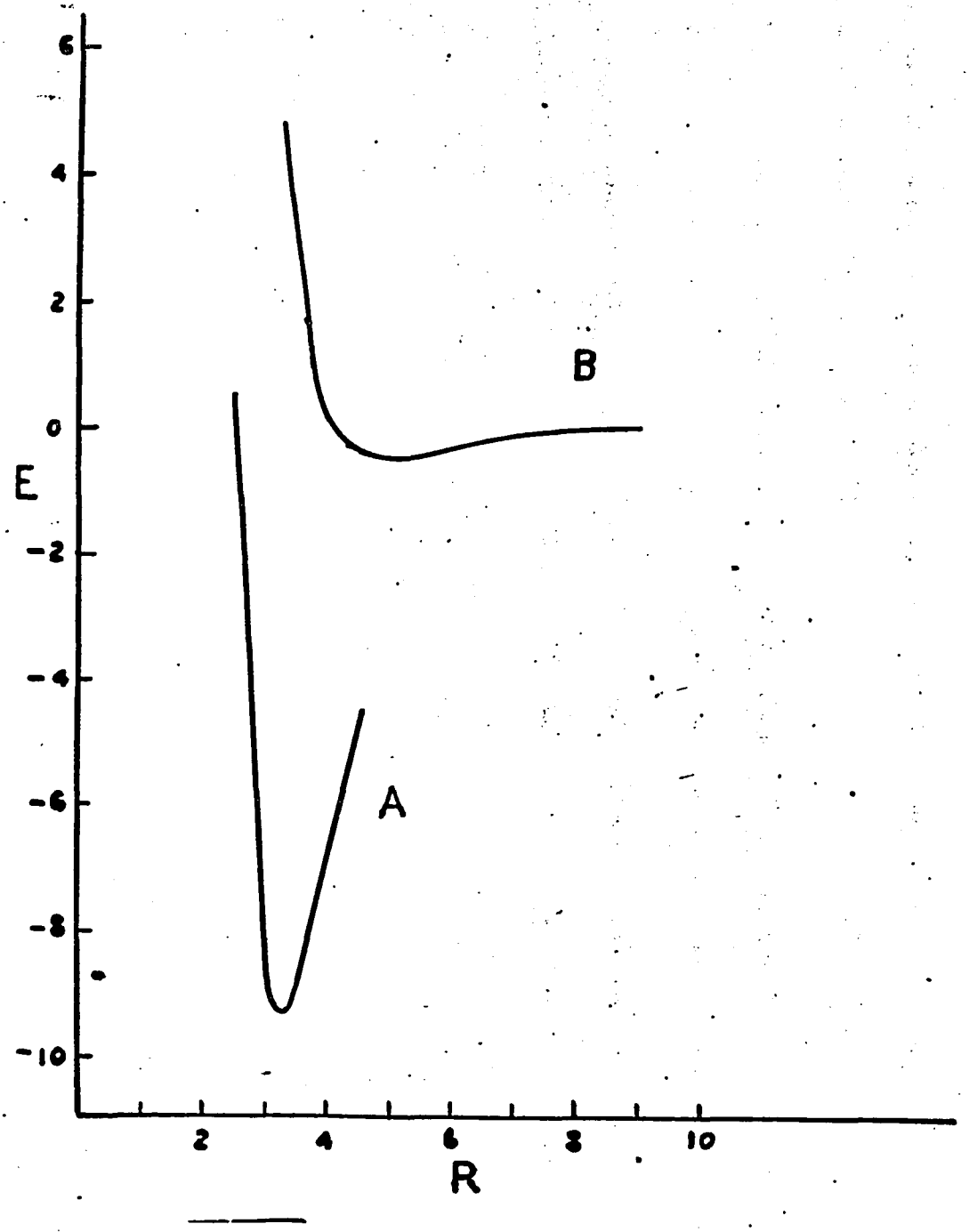

6
4
2
0
-2
-4
-6
-8
-10
E
B
A
2
4
6
8
10
R

FIGURE 7

INTERACTION ENERGY CURVES FOR $HeBe^{2+}$

(a) Theoretically calculated interaction, fit to a Born-Mayer potential.

(b) Experimentally determined interaction, fit to a Born-Mayer potential.

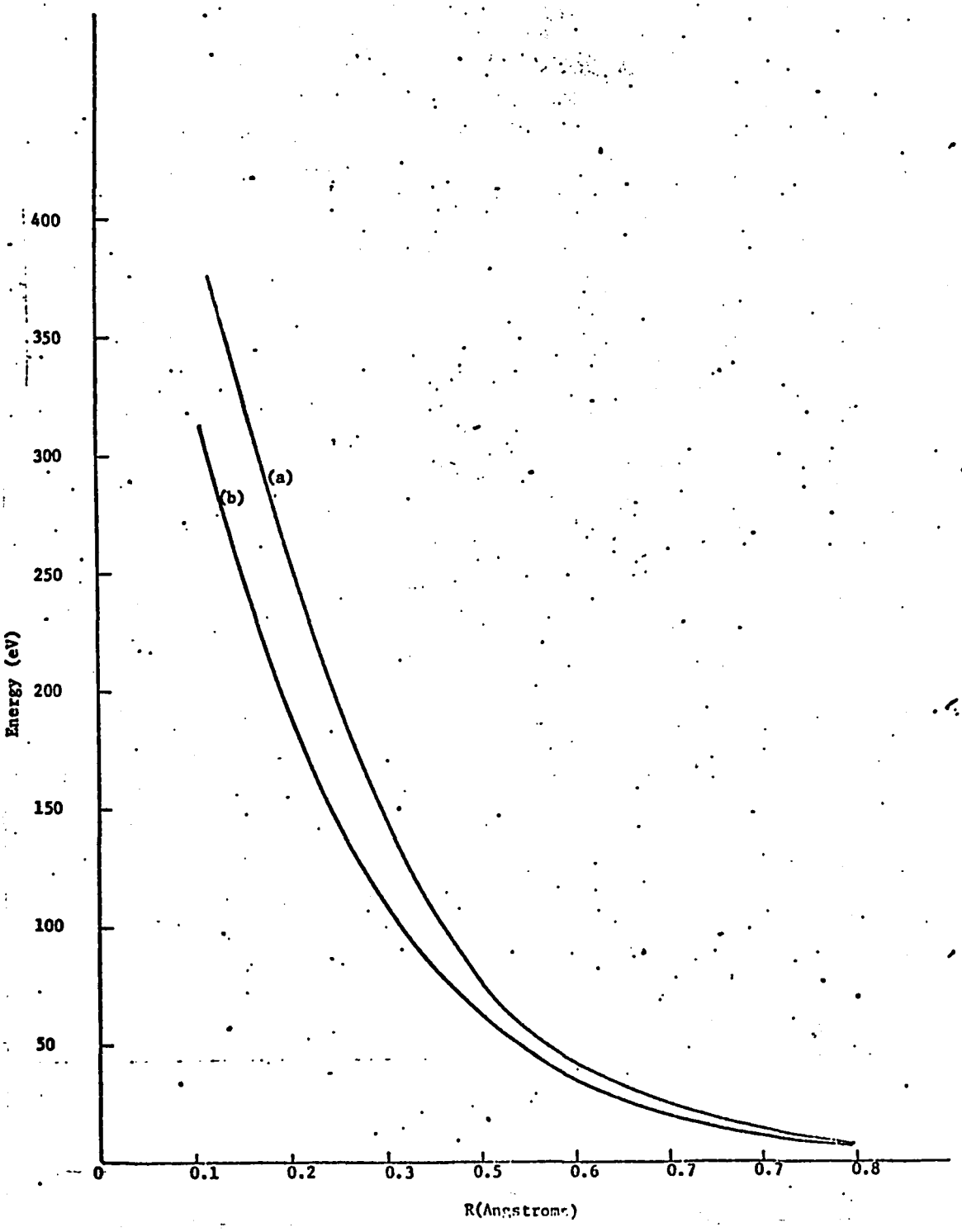
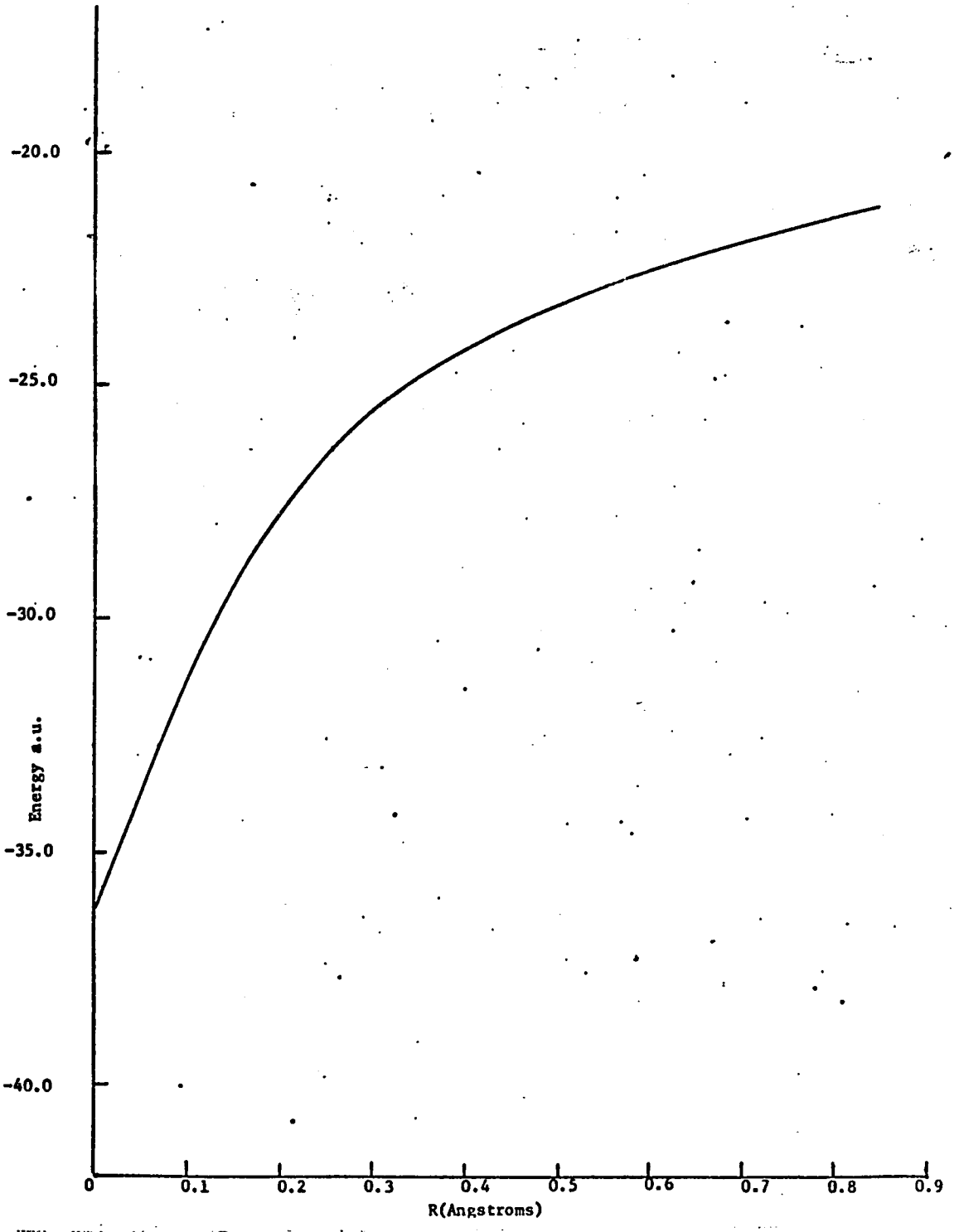

400
350
300
250
200
150
100
50
Energy (eV)
(a)
(b)
0
0.1
0.2
0.3
0.5
0.6
0.7
0.7
0.8
R(Angstrom)

FIGURE 8

TOTAL ELECTRONIC ENERGY VERSUS INTER-NUCLEAR DISTANCE FOR $BeHe^{2+}$


-20.0
-25.0
-30.0
-35.0
-40.0
Energy a.u.
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
R(Angstroms)

References

1. F. E. Niles and J. M. Heimerl, "Association, Switching and Rearrangement for Positively Charged Cluster-Ions in the Upper Atmosphere. I. Qualitative Description," Research Report, U.S. Army Ballistic Research Laboratories, Aberdeen Proving Ground, Maryland 21005.

2. C.T.R. Wilson, Trans. Roy. Soc.(London) A189, 265(1897); Phil. Trans. Roy. Soc. (London) A192,403(1899); A193, 289 (1899).

3. A. W. Castleman, Jr. and I.N. Tang, J. Chem. Phys.,57, 3629(1972).

4. L. B. Loeb, J. Aerosol Sci.,2,133 (1971).

5. C. M. York, Handbuch Der Physik (Springer, Berlin,1958), Vol. XVL, pp. 263-6.

6. A. W. Castleman, Jr., I. N. Tang, and H.R. Munkelwitz, Science, 173, 1026 (1971).

7. R. Clampitt and L. Gowland, Nature, 223, 815 (1969).

8. A. C. Aikin, Nature Phys. Sci. 235, 10 (1972).

9. V. I. Krasovskii, Sov. Astron. 2, 775 (1958)

10. B. Donn, Astrophys. J., 132, 507 (1960).

11. N.C. Wickramasinghe and V.C. Reddish, Nature, 218, 112 (1968).

12. F. Hoyle, N.C. Wickramasinghe, and V.C. Reddish, Nature, 218, 112 (1968).

13. W. Henkes, Private communication to S. Harrison.

14. P. Coffey and V.A. Mohnen, Bull. Am. Phys.Soc. 17, 392 (1972).

15. J. M. Heimerl, J. A. Vanderhoff, L.J. Puckett, G.E.Keller, and F.E. Niles, "Association, Switching, and Rearrangement for Positively Charged Cluster Ions in the Upper Atmosphere. II. Applications at 80 KM.," Research Report, U.S. Army Ballistic Research Laboratories, Aberdeen Proving Ground, Maryland 21005.

16. S.K. Searles and P. Kebarle, Cand.J.Chem.,47, 2619 (1969).

17. A. J. Cunningham, J.D.Payzant, and P. Kebarle, J.Amer. Chem. Soc., 94, 7627 (1972).

18. P.F. Knewstub and T.M. Sugden, Proc.Roy. Soc. Ser.A, 255, 520 (1960).

19. H.D. Beckey, Z. Naturforsch A, 15, 822 (1960).

20. P. F. Knewstub and A.W.Tickner, J. Chem. Phys., 38, 464 (1963).

21. R.J. Munson and A. M. Tyndall, Proc. Roy.Soc.A,172,28 (1939).

22 K.G. Spears and F.C. Fehsenfeld, J. Chem. Phys. 56,5698 (1972).

23. G.E.Keller and R.A. Beyer, J. Geophys.Res. 76,289(1971) Trans. Am. Geophys. Union 52, 303 (1971).

24. L. J. Puckett and W.C. Lineberger, Phys. Rev. A,1, 1635 (1970).

25. J. Easterfield and J. W. Linnett, Chem. Comm., 64 (1970).

26. S.S.Brenner and S.R. Goodman, Nature Phys. Sci., 235, 35 (1972).

27. E. F. Hayes and J.L. Gole, J. Chem. Phys. 55, 5132(1971).

28. D.E. Mann, G. V. Calder, K.S. Seshadri, D. White, and M.J. Linevsky, J. Chem. Phys. 46, 1138 (1967).

29. A. Buckler, J. L. Stauffer, and W. Klemperer, J. Am. Chem. Soc., 86, 4544(1964)

30. R. Clampitt and D.K. Jefferies, Nature, 226, 141 (1970).

31. L. B. Loeb, "Basic Processes in Gaseous Electronics," (University of California Press, Berkeley, 1961).

32. K. Buchheit and W. Henkes, Z. Angew. Phys. 24, 191 (1968).

33. R. Clampitt, "Cluster Ions and Ions with a Shell Structure" in "Phenomena in Ionized Gases" (Tenth International Conference) Ed. P.A. Davenport (Donald Parsons & Co., Ltd., Oxford, England , 1971).

34. I. Popescu and R. von de Heide, Z. Phys. 220,337 (1969).

35. D.C. Conway, J. Chem. Phys., 51, 5703 (1969).

36. D. C. Conway, J. Chem. Phys, 53, 1859 (1970).

37. R. E. Voshall, J. L. Pack, and A. V. Phelps, J. Chem. Phys., 43, 1990 (1965).

38. D.K. Bohme, D.B. Dunkin, F.C. Fehsenfeld, and E.E.Ferguson, J. Chem. Phys., 51, 863 (1969).

39. A.M. Hogg, R.M. Haynes, and P. Kebarle, J. Amer. Chem.Soc., 88, 28 (1968).

40. S.K. Searles and P. Kebarle, J. Phys. Chem., 72,742 (1968).

41. P. Kebarle, R. M. Haynes, and J.G. Collins, J. Amer. Chem. Soc., 89, 5735 (1967).

42. S. Geltman, Phys. Rev., 90, 808 (1953).

43. M.A. Gusinow, R.A. Gerber, and J.B.Gerardo, Phys. Rev.Lett., 25, 1248 (1970).

44. J.B. Gerardo and M.A. Gusinow, Phys. Rev. A, 3,255 (1971).

45. S. Bloom and H. Margenau, Phys. Rev., 85, 670 (1952).

46. J. L. Magee and K. Funabashi, Rad. Res., 10, 622 (1959).

47. H. Eyring, J.O.Kirschfelder, and H.S. Taylor, J. Chem. Phys., 6, 783 (1938).

48. R.D. Poshusta, and F.A. Matsen, J. Chem. Phys., 47,4795 (1967).

49. J. D. Roberts, "Notes on Molecular Orbital Calculations," (W.A. Benjamin, Inc., N.Y., 1963).

50. K.S. Pitzer, "Quantum Chemistry," (Prentice Hall, Inc., N.J., 1953).

51. D.C. Conway, J. Chem. Phys., 52, 2689 (1969).

52. D.C. Conway, and L.E. Nesbitt, J. Chem. Phys., 48, 509 (1968).

53. D.C. Conway, J. Chem. Phys., 50, 3864 (1969).

54. F.O. Ellison, J. Amer. Chem. Soc., 85, 3540 (1963).

55. G.V.Pfeiffer, N.J. Hutt, E.M. Greenwalt, and F.O. Ellison, J. Chem. Phys., 46, 821 (1967).

56. K. G. Spears, J. Chem. Phys., 57, 1850 (1972).

57. R.D. Poshusta, J. A. Haugen, and D.F. Zetik, J. Chem. Phys., 51, 5543 (1969).

58. R. E. Christofferson, J. Chem. Phys., 41, 960 (1964).

59. H. Conroy, J. Chem. Phys., 41, 1327 (1964).

61. A.G. Pearson, R.D. Poshusta, and J.C. Browne, J. Chem. Phys., 44, 1815 (1966).

62. R. F. Borkman, J. Chem. Phys.,53 , 3153 (1970).

63. I.G. Csizmadia, R. E. Kari, J.C. Polanyi, A.E. Roach, and M.A. Robb, J. Chem. Phys., 52, 6205 (1970).

64. M. E. Schwartz and L.J. Schaad, J. Chem. Phys., 48, 4709 (1968).

65. T. J. Huang, M.E. Schwartz, and G.V. Pfeiffer, J. Chem. Phys., 56, 755 (1972).

66. R.D. Poshusta and D. F. Zetik, J. Chem. Phys., 58, 118 (1972).

67. A. A. Frost, J. Phys. Chem. 72, 1289 (1968).

68. P. Kadura, Theoret. Chem. Acta., 8, 292 (1967).

69. A. A. Frost, J. Chem. Phys., 47, 3707 (1967).

70. C. Edmiston, J. Doolittle, K. Murphy, K.C. Tang, and W. Wilson, J. Chem. Phys., 52, 3419 (1970).

71. P. J. Brown and E.F. Hayes, J. Chem. Phys., 55 (1971).

72. R.D. Poshusta and W.F. Siems, J. Chem. Phys.,55, 1995 (1971).

73. R. D. Poshusta, D.W. Klint, and A. Liberles, J. Chem. Phys., 55, 252 (1971).

74. S. Fraga and B.J. Ransil, J. Chem. Phys.,37, 1112(1960).

75. W. C. Giffen and H.W. Berry, Phys. Rev. A, 3, 635 (1971).

76. C.R.Fischer, J. Chem. Phys., 48, 215 (1968).

77. B.R. Junker and J.C. Browne, "1969 Proceedings of the VI International Conference on the Physics of Electronic and Atomic Collisions" (MIT Press, Boston, Mass.,1969).

78. G.W.Catlow, M.R.C. McDowell, J.J.Kaufman, L.M. Sachs, and E.S. Chang, J. Phys. B, 3, 833 (1970).

79. F.J. Zehr and H.W. Berry, Phys. Rev., 159 , 13 (1967).

80. W.Aberth and D.C. Lorents, Phys. Rev., 182, 162 (1969).

81. D.C. Lorents and G.M. Conklin, J. Phys. B, 5, 950 (1972).

82. R. Francois, D. Dhuicq, and M. Barat, J. Phys. B, 5, 963 (1972).

83. R. McCarroll, and R.D. Piacentini, J. Phys. B, 5, 972 (1972).

84. C.C.J. Roothaan, Rev. Mod. Phys., 23, 69 (1951).

85. C.C.J. Roothaan, Rev. Mod. Phys., 32, 179 (1960

86. W.G.Richards and J.A. Horsley, "Ab Initio Molecular Orbital Calculations for Chemists" (Clarendon Press, Oxford, 1970).

87. P. O'D. Offenhartz, "Atomic and Molecular Orbital Theory," (McGraw-Hill Book Company, New York, 1970).

88. F.R. Burden and R.W. Wilson, Advances in Physics, 21, 825 (1972).

89.C.C.J. Roothaan, L.M. Sachs, and A.W. Weiss, Rev. Mod. Phys., 32, 186 (1960).

90.J.C. Slater, "Quantum Theory of Molecules and Solids," Vol. I (McGraw-Hill Book Company, New York, 1963).

91. H.F. Schaefer III, "The Electronic Structure of Atoms and Molecules, A Survey of Rigorous Quantum Mechanical Results," (Addison-Wesley Publishing Co., Inc., Reading, Mass, 1972).

92. I.G. Csizmadia, M.C. Harrison, J.W. Moskowitz and B.T. Sutcliffe, Theor. Chim. Acta, 6, 191 (1966).

93. Version 2 of this program is available from the Quantum Chemistry Program Exchange (QCPE), University of Indiana, Bloomington, Indiana.

94. L.C. Snyder and H. Basch, "Molecular Wave Functions and Properties" (J. Wiley & Sons, N.Y., 1972).

95. Dr. S. Harrison, Private Communication. See also Reference 63.

96. S.F. Boys, Proc. Roy. Soc. (London) A200, 542 (1950).

97. E.A. Mason and J.T. Varderslice, Phys. Rev. 114, 597 (1959).

98. A. van Deursen and J. Reuss, Private Communication to Dr. S. Harrison.

99. S.W. Harrison, L.J. Massa, and P. Solomon, Nature Phys. Sci., 245, 31 (1973).

100. S. Huzinaga, J. Chem. Phys.,42, 1293 (1965).

101. J. J. Kaufman and L.M. Sachs, J. Chem. Phys., 52, 3535 (1970).

102. R. A. Buckingham, Trans. Faraday Soc., 453 (1958).

103. H. Eyring, J. Walter, and G.E. Kimball, "Quantum Chemistry," (J. Wiley & Sons, Inc., N.Y. (1944).

104. R.H. Prince, Nature Phys. Sci., 242, 128 (1973).

105. C.E. Moore, Natl. Bur. Std. (U.S.) Circ. 467 (1949).

106. R.L. Brown, Astrophys. J., 174, 511 (1972).

107. S.W. Harrison, L.J. massa, and P. Solomon, Chem. Phys. Lett., 16, 57 (1972).

108. G. Herzberg, "Molecular Spectra and Molecular Structure. I. Spectra of Diatomic Molecules" (2d Edition; Princeton, N.J., D. Van Nostrand Co., Inc.)

109 C.R. Fischer, J. Chem. Phys., 42, 1293 (1968).

110. H.M. Hulbert and J.O. Hirschfelder, J. Chem. Phys., 9, 61 (1941).

111. H. Basch,M.B. Robin and N.A.Kuebler, J. Chem. Phys., 47, 1201 (1967). See also D.B. Neumann and J.W. Moskowitz, J. Chem. Phys. 50, 2216 (1969) and also Reference 94.

112. S.W. Harrison, G.A. Henderson, L. J. Massa, and P. Solomon, Astrophys. J. (To be published.)

113. W.R.Thorson, J. Chem. Phys., 41, 3881 (1964).

114. P.E. Stogryn and A.P. Stogryn, Mol. Phys., 11, 371 (1966).

115. R.V.Miller and R.D. Present, J. Chem. Phys. 38, 1179 (1963).

116. P.E. Philippson, Phys. Rev. 125, 198 (1962).

117. S.W.Harrison, L.J. Massa, and P. Solomon, J. Chem. Phys., 59, 263 (1973).

118. R.G.Parr, "The Quantum Theory of Molecular Electronic Structure," (W.A.Benjamin, Inc., Reading, Mass., 1972).

119. J.N. Murrell, S.F.A. Kettle, and J. M. Tedder, "Valence Theory" (2nd Ed., J. Wiley & Sons, N.Y., 1970).

120. J.A.Pople and D.L. Beveridge, "Approximate Molecular Orbital Theory," (McGraw-Hill Book Co., N.Y., 1970).

121. D.B.Neumann, H. Basch, R.L. Kornegay, L.C. Snyder, J.W. Moskowitz, C. Hornback, and S.P. Liebmann, "The POLYATOM System of Programs for Quantative Theoretical Chemistry: Part I,Descriptions of Programs," available from the Quantum Chemistry Program Exchange, Univ. of Ind., Bloomington, Ind.