

# Electronic structure of small metal clusters. I. Anions of $\text{Be}_2$ , $\text{Be}_3$ , and $\text{Be}_4$

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*Ab initio* calculations have been carried out for  $\text{Be}$ ,  $\text{Be}_2$ ,  $\text{Be}_3$ ,  $\text{Be}_4$ , and their anions. Whereas  $\text{Be}^-$  is unstable with respect to electron detachment,  $\text{Be}_2^-$ ,  $\text{Be}_3^-$ , and  $\text{Be}_4^-$  possess stable negative ions. The electron affinity increases with cluster size as would be expected from simple perturbation theory considerations.

## I. INTRODUCTION

The physical and chemical behavior of small metal clusters is presently of much interest<sup>1</sup> primarily because of the utility of such species as chemical reaction catalysts. Of fundamental importance in this area is the nature of the interaction of the metal clusters with adsorbed atoms or molecules. To fully understand the combined adsorbate-cluster system it is essential that one have knowledge of the electronic structures (charge densities, valence orbital energies, etc.) of both the adsorbate and the cluster. The emphasis of the present work is directed toward developing, through the study of prototype systems, an understanding of the electron accepting properties of small clusters. In particular, we address questions of stability of the cluster anions with respect to both electron loss and dissociation as well as the spatial distributions of the anions' electron densities. It is our belief that the extension of this kind of investigation to a wide range of metal aggregates will yield valuable new electronic structure information which is directly related to the behavior of clusters both in adsorption and oxidation-reduction processes. Of course, the ultimate goal of such an undertaking is to aid in the design of clusters whose physical and chemical properties (e.g., electron affinities, ionization potentials, and tendency toward chemisorption) are optimal for specific catalytic processes. A firmly-based knowledge of the valence orbital structure of various metal clusters will eventually permit this goal to be achieved.

In this investigation of the electron accepting behavior of small clusters, we have chosen beryllium as our prototype system although beryllium itself is not of great catalytic interest. This choice was made for several reasons. There already exists in the literature good quality *ab initio* results<sup>2</sup> on both the stability of neutral  $\text{Be}_n$  clusters ( $n \leq 22$ ) and the interaction of H atoms with these clusters. Of course, the fact that each Be atom contains only four electrons makes *ab initio* molecular orbital calculations on small Be clusters computationally tractable. In addition, the interaction of H with Be clusters has been investigated by Companion<sup>3</sup> using the semi-empirical CNDO/2 method. Companion's study suggested

the possibility that Be clusters have an appreciable electron affinity (EA). Finally, our own work<sup>4</sup> on  $\text{Be}_2^-$ , in which we predicted the anion to be stable with respect to the unbound neutral  $\text{Be}_2$  for a range of internuclear distances (e.g., by 0.29 eV at an internuclear separation of 4.62 a.u.), motivated us to consider the possible stability of the anions of larger Be clusters.

The results of the present investigation provide prototypical information about clusters of other atoms with the  $ns^2np^0$  electronic configuration (e.g., Mg, Zn, Cd, and Hg). For clusters containing these heavier elements, the role of *d*-like atomic orbitals will quite likely be important. Because such orbitals do not contribute significantly to the bonding in Be clusters, the present study will yield no information on their effects. Our future research on Mg clusters and mixed MgBe clusters will allow us to address this important question. In Sec. II of this paper we discuss the basis sets and computational procedures employed in the present work. Section III contains an analysis of our results, our suggestions concerning possible mechanisms of formation of these anions, and a brief description of plans for future work in this area.

## II. CALCULATIONAL DETAILS

In an earlier study<sup>4</sup> of  $\text{Be}_2^-$  we constructed a Slater-type orbital (STO) basis set suitable for the description of both the neutral and anionic species. This basis set was formed by augmenting a double-zeta quality basis with two sets of more diffuse *s* and *p<sub>σ</sub>* atomic orbitals as well as one set of diffuse *p<sub>π</sub>* functions. In the present work, we employ a comparable basis of 11 contracted Gaussian-type orbitals (GTO) which gives a somewhat higher total energy than our STO basis for  $\text{Be}_2$  and the Be atom at both the self-consistent-field (SCF) and second-order Rayleigh-Schrödinger correlation levels of treatment. This basis, which is described in Table I, consists of 5 *s* and 2 *p* (*p<sub>x</sub>*, *p<sub>y</sub>*, and *p<sub>z</sub>*) functions and was constructed by modifying the 6-31G Be basis set of Binkley and Pople<sup>5</sup> to provide the flexibility to describe both the neutral and anionic clusters. All the calculations reported in the present study have been carried out using this GTO basis on each Be atom.

In performing the calculations described below, the MOLECULE Gaussian program<sup>6</sup> was employed to generate

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TABLE I. Beryllium atom contracted Gaussian basis set.<sup>a</sup>

Type	Exponents	Contraction coefficients
1s	1264.5857	0.001945
	189.9368	0.014835
	43.1590	0.072090
	12.0987	0.237154
	3.8063	0.469199
	1.2729	0.356520
1s'	0.7478	1.0
1s''	0.2200	1.0
1s'''	0.0823	1.0
1s <sup>iv</sup>	0.0300	1.0
2p	3.1965	0.055980
	0.7478	0.261551
	0.2200	0.793972
2p'	0.0500	1.0

<sup>a</sup>This basis set is a modification of the 6-31G basis set of Binkley and Pople (Ref. 5). The 1s function is the same as that of Binkley and Pople and we have used a scale factor of 1.03 for the 2s and 2p functions. Further, we split off the three components of the 2s functions; the 2s function with exponent 3.1965 did not contribute significantly to the bonding of Be<sub>2</sub> and, hence, was neglected. Finally, we have increased the flexibility of the basis set by employing diffuse 1s''' and 1s<sup>iv</sup> functions rather than the single 2s' function of the 6-31G basis set.

one- and two-electron integrals. For the neutral clusters Be, Be<sub>2</sub>, Be<sub>3</sub> (linear), Be<sub>3</sub> (triangular), and Be<sub>4</sub> (tetrahedral), a restricted Hartree-Fock (RHF) calculation was used to calculate the total energies; second-order Rayleigh-Schrödinger correlation corrections were evaluated for Be and Be<sub>2</sub> in order to obtain a crude estimate of these effects. The energies of the anions were obtained by carrying out spin-unrestricted Hartree-Fock (UHF) calculations. Hence, the majority of the EA's reported here are of  $\Delta$ SCF (the difference between the neutral's RHF energy and the UHF energy of the anion) quality; orbital relaxation effects are taken into consideration but correlation effects are neglected except for Be<sub>2</sub>. For Be<sub>2</sub> we calculated an EA including both second-order and third-order correlation effects. By comparing this correlated EA for Be<sub>2</sub> (0.31 eV with our present GTO basis set and 0.29 eV for our earlier STO basis set) with the present  $\Delta$ SCF prediction (0.21 eV), we estimate that the inclusion of electron correlation effects would increase the EA's of the clusters studied here by approximately 0.05 eV per Be atom.<sup>7</sup> The use of larger, more flexible basis sets might result in an additional increase of a similar magnitude in the EA's. Thus, our prediction of the cluster EA's may be in error by as much as 0.1 eV per Be atom. However, because each cluster anion is likely to have more correlation energy than the respective neutral cluster, the predicted  $\Delta$ SCF-level EA's are expected to be too small. Thus, we feel that in those cases for

which we predict the cluster anion to be stable relative to the neutral, the anion is indeed stable. The amount of stability may be underestimated by as much as 0.3–0.4 eV for the three and four atom clusters (this error estimate includes consideration of finite basis set effects as well as correlation energy corrections). With these limitations of the calculations in mind, let us now turn to discuss the Be atom and Be<sub>2</sub>, Be<sub>3</sub>, and Be<sub>4</sub> and their anions in detail.

### A. Be atom

Using the (10s4p/5s2p) GTO basis set given in Table I, we obtained an SCF energy of -14.5648 a.u. and a second-order (Rayleigh-Schrödinger) correlation energy of -0.1418 a.u. for the Be atom. For comparison, we note that Dykstra, Schaefer, and Meyer<sup>26</sup> using a (9s4p/5s2p) GTO basis set obtained an SCF energy of -14.5723 a.u. The Be correlation energy has been calculated by Bunge<sup>8</sup> to be -0.0943 a.u. It is not surprising that a Rayleigh-Schrödinger correlation energy estimate is considerably larger than Bunge's accurate value; second-order perturbation theory is well known to overestimate correlation energies. The Hartree-Fock limit<sup>9</sup> energy of Be is -14.5730 a.u. Thus, our basis yields an SCF energy for Be which lies 0.0075 a.u. above that obtained by Dykstra *et al.* using the same size basis. Our 5s2p basis set was chosen to provide a relatively good description of both Be<sub>2</sub> and Be<sub>2</sub><sup>-</sup>. To gain the flexibility required to adequately describe Be<sub>2</sub><sup>-</sup> and the larger cluster anions within such a moderately sized basis set, we had to settle for somewhat higher energies for the neutral species than those obtained by Dykstra *et al.*

Our calculations, using contracted basis sets as large as 5s4p and allowing for both second- and third-order correlation effects, have indicated that the (1s<sup>2</sup>2s<sup>2</sup>2p) <sup>2</sup>P state of Be<sup>-</sup> is unstable with respect to neutral Be. We find no evidence for a stable (1s<sup>2</sup>2s<sup>2</sup>3s) <sup>2</sup>S state of Be<sup>-</sup> which has, on the basis of isoelectronic extrapolation, been claimed<sup>10,11</sup> to be bound by as much as 0.7 eV.<sup>12</sup> In this respect, our findings are in agreement with the large CI calculation of Weiss.<sup>13</sup> On the basis of evidence from electron transmission spectroscopy<sup>15</sup> showing that the <sup>2</sup>P shape resonances of Mg, Cd, Zn, and Hg are unstable by 0.15–0.40 eV, we expect that <sup>2</sup>P Be<sup>-</sup> will exist as a shape resonance<sup>14</sup> and will be unstable by 0.1–0.5 eV with a lifetime of 10<sup>-14</sup>–10<sup>-15</sup> sec. The primary purposes for carrying out the calculations on the Be atom were to assess the quality of our basis set and to obtain an SCF energy for the atom to use in our estimations of the dissociation energies of the Be clusters. Questions concerning the stability of Be<sup>-</sup> are important primarily in connection with the dissociation behavior of the cluster anions. Due to the resonance nature of the <sup>2</sup>P state of Be<sup>-</sup>, it is not possible to calculate its properties from a straightforward variational procedure; however, we, in collaboration with Kaiser and Purvis, have recently performed<sup>16</sup> stabilization calculations<sup>17</sup> on this system. The results of these calculations are not sufficiently accurate to reliably predict the position and width of the <sup>2</sup>P shape resonance. However, we can say that these calculations also gave no evidence for either a stable <sup>2</sup>P or <sup>2</sup>S state of Be<sup>-</sup>.

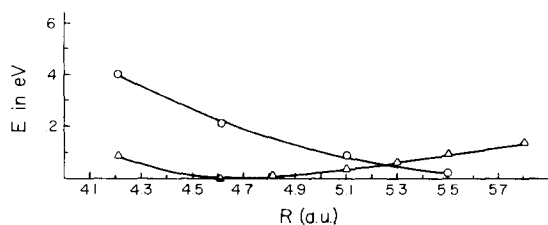


FIG. 1. Potential energy curves of the  $X^1\Sigma_g$  state of  $\text{Be}_2$  (RHF) ( $\circ$ ) and the  $X^2\Sigma_g$  state of  $\text{Be}_2^-$  (UHF) ( $\Delta$ ).

## B. $\text{Be}_2$

Our earlier calculation using a STO basis set gave a total (SCF) energy of  $-29.1218$  a. u. for the  $(1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2)$   $X^1\Sigma_g$  state of  $\text{Be}_2$  at internuclear separation ( $R$ ) of 4.60 a. u. The present GTO basis yields SCF energies of  $-29.1205$  and  $-29.1281$  a. u., respectively, for the  $X^1\Sigma_g$  neutral and  $(1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 3\sigma_g)$   $X^2\Sigma_g$  anion species at approximately this same internuclear distance (4.62 a. u.). With our present Gaussian basis, the  $\Delta\text{SCF}$  vertical ( $R = 4.62$  a. u.) EA of 0.21 eV compares well with our earlier correlated prediction of 0.29 eV. Employing essentially the same equation-of-motion method<sup>18</sup> as was used in our earlier investigations and using the GTO basis set given in Table I, we obtained a correlated EA of 0.31 eV. As in the STO study, the  $(1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 1\pi_u)$   $^2\Pi_u$  state of  $\text{Be}_2^-$  is not predicted to be stable to electron detachment at this bond length. The correlated calculations indicate that the  $^2\Sigma_g$  state of  $\text{Be}_2^-$  lies below the  $^1\Sigma_g$  state of  $\text{Be}_2$  for values of  $R$  out to 5.80 a. u. at which point the curves cross; for larger  $R$  the electron can autodeattach. In the GTO SCF calculations the crossing point of the  $^2\Sigma_g$   $\text{Be}_2$  and  $^2\Sigma_g$   $\text{Be}_2^-$  curves occurs at 5.25 a. u., and the potential well of  $\text{Be}_2^-$  is shallower than when correlation effects are treated. The  $\text{Be}_2$  and  $\text{Be}_2^-$  potential energy curves are presented in Fig. 1.

The interaction of the  $p$  orbitals on the two Be atoms gives rise to two bonding and two antibonding molecular orbitals (MO's):  $3\sigma_g$ ,  $1\pi_u$ ,  $3\sigma_u$ , and  $1\pi_g$ , leading us to expect that  $\text{Be}_2$  will possess four low-lying negative ion states corresponding to the attachment of an electron to any one of these four orbitals. For  $R = 4.62$  a. u. the anions formed by occupation of the  $3\sigma_u$ ,  $1\pi_u$ , and  $1\pi_g$  orbitals should be unstable to electron detachment and correspond to shape resonances. There should also be several low-lying Feshbach resonance-type anions arising from the  $1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 xy$  configuration, where  $x$  and  $y$  stand for any of the  $3\sigma_g$ ,  $3\sigma_u$ ,  $1\pi_g$ , and  $1\pi_u$  MO's.

Because the  $^2P$  state of Be lies only 2.7 eV above the  $^2S$  ground state and because the presence of the low lying  $p$  orbitals is responsible for the importance of  $sp$  hybridization in many Be compounds, we treat the four molecular orbitals resulting from the  $2p$  atomic orbitals as valence orbitals.<sup>19</sup> Once the "extra" electron is added to any  $\text{Be}_n$  cluster, the  $2p$  orbitals have to be thought of as partially occupied and, hence, they are truly valence orbitals.

Classical MO theory predicts that the  $^1\Sigma_g$  ground state

of  $\text{Be}_2$  is repulsive since  $\text{Be}_2$  has the same number of bonding and antibonding electrons. Because the ground state of  $\text{Be}_2$  has not been detected experimentally, it appears that the van der Waals minimum is very shallow ( $\leq 1$  kcal/mol); it may even be too shallow to support vibrational levels. The large-scale CI calculations of Bender and Davidson<sup>20</sup> failed to yield a minimum in this potential curve. More recently, Dykstra *et al.*<sup>2(c)</sup> found that the  $\text{Be}_2$  ground state curve is repulsive in a SCF calculation, whereas the molecule was bound by 0.13 kcal in a calculation including correlation effects. The fact that our SCF calculations also yield a totally repulsive curve for  $\text{Be}_2$  is a significant observation since, if a minimum were obtained in this case, it would probably have indicated that our basis was allowing one atom to utilize the basis functions centered on the other atom to improve its atomic orbitals. Thus, the absence of a minimum in our SCF-level curve is evidence in support of the flexibility of our basis set.

When, in Secs. II.C and II.D, we examine the 3 and 4 atom clusters, we will be especially interested in their electronic charge densities. In particular, we will examine both the relative importance of  $s$  and  $p$  functions in the various valence molecular orbitals as well as the diffuseness of the molecular orbitals. Therefore, for purposes of comparison, it will be useful to examine more closely the valence orbitals of  $\text{Be}_2$ . In Table II we list the expansion coefficients of the  $2\sigma_g$ ,  $2\sigma_u$ , and  $3\sigma_g$  valence orbitals of  $\text{Be}_2$  and  $\text{Be}_2^-$  (for the calculation carried out at 4.62 a. u.). The  $2\sigma_g$  and  $2\sigma_u$  orbitals are described (as expected) predominantly by the bonding and antibonding combinations, respectively, of the Be  $2s$  orbitals. We also note that the  $2\sigma_u$  orbitals of the anion have a larger contribution from the atomic  $2p$  functions than does the  $2\sigma_u$  orbital of the neutral species. The  $3\sigma_g$  orbital is essentially the bonding combination of the  $2p$  orbitals (along the internuclear axis) while the  $1\pi_u$  orbital (not given in Table II) results from the bonding combination of the  $2p$  orbitals perpendicular to the intermolecular axis.

At sufficiently small internuclear separations, both the bonding  $3\sigma_g$  and  $1\pi_u$  orbitals should acquire negative orbital energies. Indeed, we find that the  $3\sigma_g$  orbital acquires a negative orbital energy for  $R \leq 3.5$  a. u., whereas  $1\pi_u$  orbital energy becomes negative for  $R \leq 3.1$  a. u. It is likely that at somewhat smaller internuclear separations the  $1\pi_u$  orbital would fall below the  $3\sigma_g$  orbital. The higher-lying  $1\pi_g$  and  $3\sigma_u$  orbitals, which are of antibonding nature, will not be discussed in detail here.

Although  $^2\Sigma_g \text{Be}_2^-$  is stable at  $R = 4.62$  a. u., as was demonstrated by our  $\Delta\text{SCF}$  and correlated calculations, it is not stable at a Koopmans' theorem<sup>21</sup> level of description. That is, in a frozen core approximation,  $^2\Sigma_g \text{Be}_2^-$  is predicted to lie above  $^1\Sigma_g \text{Be}_2$  and, hence, corresponds to a resonance<sup>22</sup> (as does the  $^2\Pi_u$  state). In general, the nature of virtual orbitals with positive orbital energies is strongly dependent on the diffuseness of the basis functions. For example, if we were to add more and more diffuse  $s$  and  $p$  functions to the basis set for  $\text{Be}_2$ , then we would find  $\sigma_g$  and  $\pi_u$  virtual orbitals with energies approaching zero (at  $R = 4.62$  a. u.). The resulting very dif-

TABLE II. Orbital energies and coefficients of the  $2\sigma_g$ ,  $2\sigma_u$ , and  $3\sigma_g$  molecular orbitals of  $X^1\Sigma_g^-$   $\text{Be}_2$  and  $X^2\Sigma_g^-$   $\text{Be}_2^-$  at  $R=4.62$  a.u.<sup>a</sup>

Atomic /orbital function/energy (a.u.)	$\text{Be}_2$			$\text{Be}_2^-$				
	$2\sigma_g$	$2\sigma_u$	$3\sigma_g$	$2\sigma_g\alpha$	$2\sigma_g\beta$	$2\sigma_u\alpha$	$2\sigma_u\beta$	$3\sigma_g\alpha$
	-0.396	-0.241	0.011	-0.226	-0.185	-0.097	-0.035	-0.030
$1s^b$	-0.158	-0.155	-0.005	-0.149	-0.148	-0.127	-0.137	-0.021
$1s'$	-0.092	-0.089	-0.009	-0.089	-0.082	-0.076	-0.076	-0.012
$1s''$	0.321	0.292	0.044	0.289	0.268	0.250	0.224	0.037
$1s'''$	0.322	0.498	-0.085	0.312	0.285	0.230	0.468	0.061
$1s^{iv}$	0.046	0.221	0.410	0.054	0.111	0.208	0.842	0.301
$2p_x$	-0.106	0.082	0.290	-0.156	-0.092	0.141	0.057	0.335
$2p'_x$	-0.017	0.037	0.418	-0.018	-0.039	0.268	-0.193	0.398

<sup>a</sup>The internuclear axis is chosen to lie in the  $x$  direction; the coordinates of the atoms are  $x=2.31$  and  $-2.31$  a.u.

<sup>b</sup>The coefficients are only given for the atom at  $x=2.31$  a.u.; those for the other atom are determined by symmetry.

fuse MO's would be approximating the continuum. We are not really interested in the general behavior of the continuum but rather in knowing the location of the resonances embedded in the continuum. Hence, we would like to be able to find those molecular orbitals which correspond to the resonances. In principle, one could locate the positions of the resonances of  $\text{Be}_2$  as well as the  $^2P$   $\text{Be}^-$  shape resonance by means of a stabilization calculation<sup>17</sup> or from a scattering calculation. These procedures involve elaborate calculations and are very expensive. Although we have not carried out a stabilization calculation for  $\text{Be}_2^-$ , we believe that our lowest  $3\sigma_g$ ,  $3\sigma_u$ ,  $1\pi_u$ , and  $1\pi_g$  orbitals (as well as our  $2p$  orbital of Be) are close to the "correct" stabilized orbitals. In the sense that we have chosen the orbital exponents of the diffuse functions in our  $5s2p$  GTO basis set to provide an optimal UHF description of  $^2\Sigma_g^- \text{Be}_2^-$ , the  $3\sigma_g$ ,  $3\sigma_u$ ,  $1\pi_u$ , and  $1\pi_g$  virtual orbitals of  $\text{Be}_2$  are systematically determined and may be considered as corresponding to the frozen core (static exchange) scattering states.

In Figs. 2(a), 2(b), and 2(c) we plot, respectively, the charge densities along the internuclear axis of the  $2\sigma_g$ ,  $2\sigma_u$ , and  $3\sigma_g$  RHF orbitals of  $\text{Be}_2$  for a bond length of 4.62 a.u. For the  $3\sigma_g$  orbital we have also given the contour map [Fig. 2(d)], i.e., we have plotted  $|\psi(x, y, z)|^2 = c$ , for  $c = 0.0025, 0.0050, 0.010, 0.020, \text{ and } 0.040$ . Figure 1(a) displays very clearly the bonding contribution of the  $2p$  atomic orbitals to the  $2\sigma_g$  molecular orbital.

### C. Linear and triangular $\text{Be}_3^-$

Using the same  $5s2p$  GTO basis set on each Be atom, we performed RHF calculations on linear and triangular (equilateral)  $\text{Be}_3$  and UHF calculations on the lowest sigma and pi states of the corresponding anions. Calculations were carried out at several interatomic distances in order to determine the equilibrium geometries of the anions and neutrals as well as the adiabatic EA's of these two forms of  $\text{Be}_3$ . Due to limitations on the availability of

computer time, we restricted our search to the symmetric stretch mode of the linear  $\text{Be}_3$  and the symmetric breathing mode of triangular  $\text{Be}_3$ .

Our SCF calculations on linear  $\text{Be}_3$  indicated a dissociative  $^1\Sigma_g^+$  ground state out to  $R=4.8$  a.u. On the other hand, we found the  $^2\Sigma_u$  state of the anion to be bound and more stable than the ground state of the neutral by 0.98 eV at the anion's equilibrium bond length of  $R=4.52$  a.u. Moreover, the  $^2\Pi_u$  state of linear  $\text{Be}_3^-$  is predicted to be stable by 0.33 eV at  $R=4.62$  a.u. and to have an equilibrium bond length of 4.42 a.u.

For linear  $\text{Be}_3$ , the three interacting  $2p$  orbitals on each Be atom give rise to two  $\sigma_u$ , one  $\sigma_g$ , one  $\pi_g$ , and two  $\pi_u$  molecular orbitals. Of these, we are particularly interested in the  $3\sigma_u$  and  $1\pi_u$  orbitals, which, upon occupation by an electron, give rise to the two stable anion states described above. The expansion coefficients of the  $3\sigma_g$ ,  $4\sigma_g$ ,  $5\sigma_g$ ,  $2\sigma_u$ ,  $3\sigma_u$ , and  $1\pi_u$  orbitals are given in Table III. Although the  $3\sigma_g$ ,  $4\sigma_g$ , and  $2\sigma_u$  orbitals are dominated by contributions from the interaction of the Be  $2s$  atomic orbitals, all three of these MO's also contain an appreciable admixture of the atomic  $2p$  functions. The lowest unoccupied molecular orbital (LUMO) (the  $3\sigma_u$  orbital) of linear  $\text{Be}_3$  is bound by 0.42 eV (in the RHF calculation) at the equilibrium geometry of linear  $\text{Be}_3^-$  and the lowest energy  $\pi_u$  virtual orbital is nearly bound.

In Fig. 3 we display the contour maps for the valence orbitals obtained from the RHF calculation on the neutral  $\text{Be}_3$  for a bond length of 4.62 a.u. The contour plots make quite clear the increase, in comparison with the occupied valence orbitals of  $\text{Be}_2$ , in the bonding nature of the  $3\sigma_g$ ,  $2\sigma_u$ , and  $4\sigma_g$  occupied orbitals due to the contributions from the atomic  $p$  functions. This is particularly striking in the case of the  $2\sigma_u$  orbital which would be nonbonding in a calculation employing only  $s$  functions on the Be atoms. From Fig. 3(b) we see that, due to the  $p$  functions on the central atom, this orbital is actu-

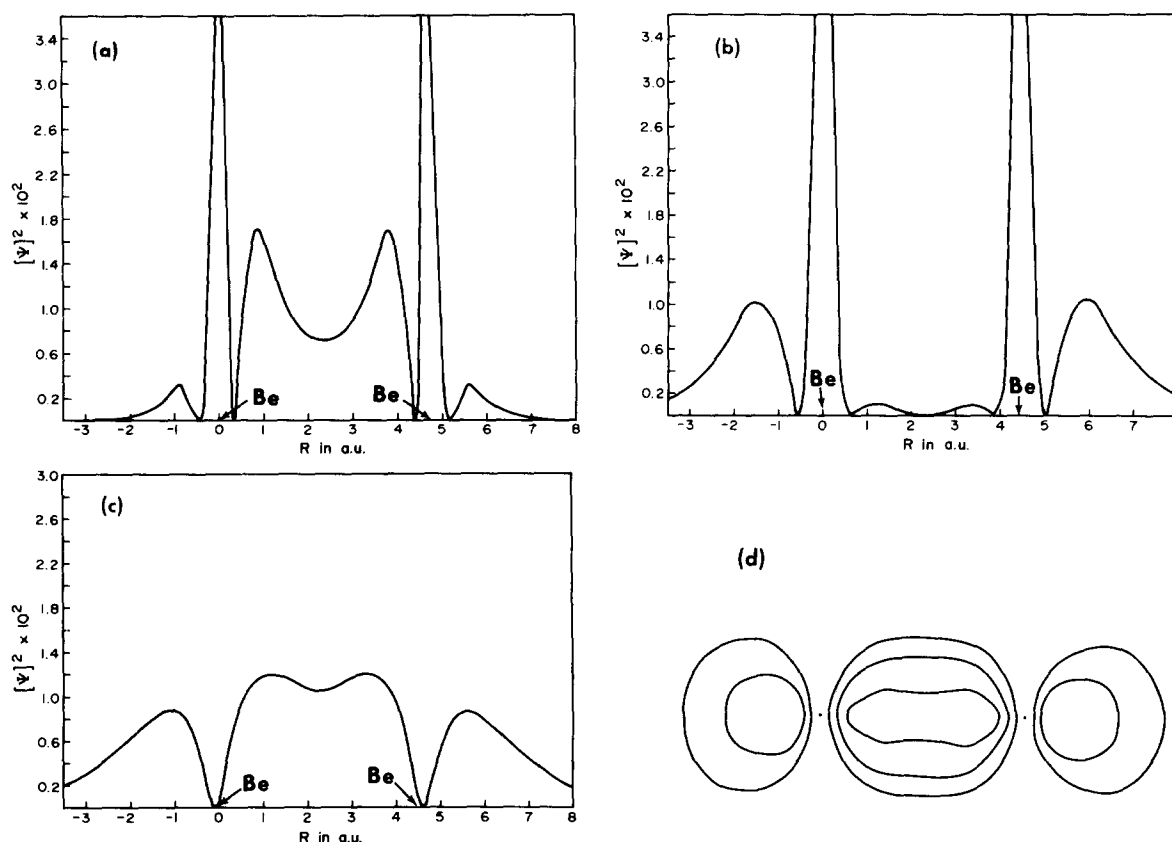


FIG. 2. Charge density along the internuclear axis of RHF molecular orbitals of  $\text{Be}_2$ : (a)  $2\sigma_g$ , (b)  $2\sigma_u$ , and (c)  $3\sigma_g$ . The Be atoms are located at  $R=0$  and  $4.62$  a.u. In (d) we plot the contour map of the  $3\sigma_g$  orbital. The contour lines  $|\psi(x, y, 0)|^2 = c$ , are shown for  $c=0.0025, 0.0050, 0.010, 0.020, \text{ and } 0.040 e/a_0^3$ .

ally fairly strongly bonding. The  $3\sigma_g$ ,  $2\sigma_u$ , and  $4\sigma_g$  orbital energies are  $-0.418$ ,  $-0.344$ , and  $-0.200$  a.u., respectively, at  $R=4.62$  a.u. as compared to the values of  $-0.344$  and  $-0.200$  a.u. for the  $2\sigma_g$  and  $2\sigma_u$  orbitals of

$\text{Be}_2$  at  $R=4.62$  a.u. The  $2s$  orbital energy of Be is  $-0.311$  a.u. The mean energy of the  $2\sigma_g$  and  $2\sigma_u$  orbital energies of  $\text{Be}_2$  is  $-0.318$  a.u. while the mean of the  $3\sigma_g$ ,  $2\sigma_u$ , and  $4\sigma_g$  orbital energies of linear  $\text{Be}_3$  is  $-0.321$  a.u.

TABLE III. Orbital energies and coefficients of the valence molecular orbitals of linear  $\text{Be}_3$ .<sup>a</sup>

	$3\sigma_g$	$2\sigma_u$	$4\sigma_g$	$3\sigma_u$	$1\pi_u$	$5\sigma_g$
Atomic function/orbital energy (a.u.)	$-0.418$	$-0.344$	$-0.200$	$-0.013$	$0.006$	$0.074$
$1s^b$	$-0.173$	...	$0.129$	...	...	$-0.019$
$1s'$	$-0.103$	...	$0.076$	...	...	$0.022$
$1s''$	$0.350$	...	$-0.237$	...	...	$-0.151$
$1s'''$	$0.355$	...	$-0.494$	...	...	$0.768$
$1s^{iv}$	$0.002$	...	$-0.250$	...	...	$-0.738$
$2p$	...	$0.209$	...	$-0.289$	$0.230$	...
$2p'$	...	$0.264$	...	$-0.820$	$0.448$	...
$1s^c$	$-0.102$	$-0.149$	$-0.118$	$-0.027$	...	$-0.066$
$1s'$	$-0.061$	$-0.091$	$-0.067$	$-0.012$	...	$-0.004$
$1s''$	$0.210$	$0.316$	$0.212$	$0.020$	...	$-0.083$
$1s'''$	$0.188$	$0.248$	$0.413$	$0.269$	...	$1.014$
$1s^{iv}$	$0.032$	$-0.011$	$0.248$	$0.655$	...	$-0.910$
$2p$	$-0.088$	$-0.057$	$0.126$	$0.253$	$0.151$	$-0.043$
$2p'$	$-0.017$	$0.058$	$0.071$	$0.190$	$0.291$	$0.016$

<sup>a</sup>The internuclear axis is chosen to lie in the  $x$  direction. The  $2p$  orbitals in this table refer to  $2p_x$  in the case of the  $\sigma$  orbitals and  $2p_y$  in the case of one of the members of a degenerate  $\pi$  state and  $2p_z$  for the other. The three atoms are located at  $x=4.62, 0, 0, \text{ and } 4.62$  a.u.

<sup>b</sup>This set of functions is centered on the middle atom (at  $x=0, 0$ ).

<sup>c</sup>This set of functions is centered on the atom at  $x=4.62$  a.u. The coefficients for the atom at  $-4.62$  a.u. are given by symmetry.

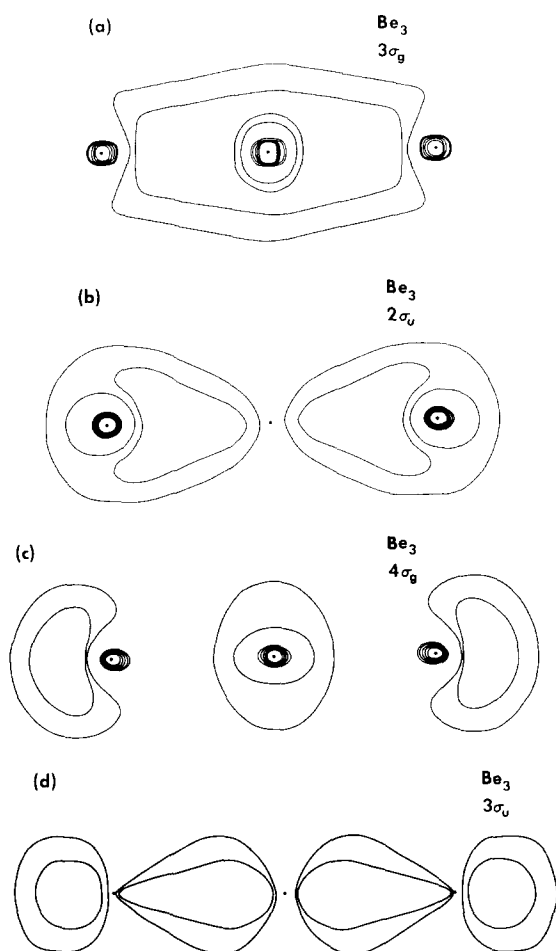


FIG. 3. Charge density maps of selected RHF molecular orbitals of linear  $\text{Be}_3$ : (a)  $3\sigma_g$ , (b)  $2\sigma_u$ , and (c)  $4\sigma_g$ . The contour lines  $|\psi(x, y, 0)|^2 = c$  are shown for  $c = 0.0025, 0.0050, 0.010, 0.020$ , and  $0.040 e/a_0^3$ . The nearest neighbor bond lengths are 4.62 a.u.

For comparison we also note that the mean of orbital energies of the occupied valence orbitals of equilateral  $\text{Be}_3$  and tetrahedral  $\text{Be}_4$  was found to be  $-0.328$  and  $-0.350$  a.u., respectively. The decreasing value of this mean with increasing cluster size reflects the corresponding increase in the bonding nature of the orbitals which is brought about by the  $p$  atomic functions. The mean orbital energy of the  $3\sigma_g$  and  $4\sigma_g$  orbitals of linear  $\text{Be}_3$  is  $-0.309$  a.u., which indicates that the  $2\sigma_u$  orbital of  $\text{Be}_3$  is largely responsible for the lowering of the mean orbital energy relative to the  $2s$  orbital energy of Be.

So far we have only considered negative ions formed by the addition of an electron to the  $3\sigma_u$  or  $1\pi_u$  orbitals. Since these two orbitals are strongly bonding, there arises the possibility that one or more of the negative ion states arising from the  $(3\sigma_g^2 2\sigma_u^2 4\sigma_g 3\sigma_u^2)$ ,  $(3\sigma_g^2 2\sigma_u^2 4\sigma_g 1\pi_u^2)$ , and  $(3\sigma_g^2 2\sigma_u^2 4\sigma_g 3\sigma_u 1\pi_u)$  configurations could be stable. In each of these configurations, one of the parent's electrons has been promoted from the antibonding  $4\sigma_g$  orbital into a bonding orbital, and the "extra" electron is also added to a bonding orbital. In connection with these investigations of excited states of the  $\text{Be}_3^-$  anion, we carried out SCF calculations on the  $(3\sigma_g^2 2\sigma_u^2 4\sigma_g 3\sigma_u)^3\Sigma_u$  and  $(3\sigma_g^2 2\sigma_u^2 4\sigma_g 1\pi_u)^3\Pi_u$  states of the neutral  $\text{Be}_3$  and found

that both states lie only about 1 eV above the ground state, thereby making plausible the possibility of stable Feshbach anion states. We, therefore, performed (at  $R = 4.42$  a.u., because of the increased likelihood of energetically favorable  $\pi$  states) UHF calculations on the three anion states listed below.

The  $(3\sigma_g^2 2\sigma_u^2 4\sigma_g 3\sigma_u^2)$  configuration of  $\text{Be}_3^-$  gives rise to a  $^2\Sigma_g^-$  anion state which we find to be bound relative to electron loss, by 0.27 eV in our  $\Delta$ SCF calculation. The  $(3\sigma_g^2 2\sigma_u^2 4\sigma_g 3\sigma_u 1\pi_u)$  configuration gives rise to two  $^2\Pi_g$  and one  $^4\Pi_g$  state. The  $^4\Pi_g$  state is calculated to be bound by 1.75 eV. On the basis of Hund's rules, we expect that the  $^2\Pi_g$  states are less stable than the  $^4\Pi_g$  species. However, the  $^2\Pi_g$  states cannot be treated within a single determinantal UHF scheme and are, therefore, not included in our present study. The  $(3\sigma_g^2 2\sigma_u^2 4\sigma_g 1\pi_u^2)$  configuration gives rise to  $^2\Sigma_g^+$ ,  $^2\Sigma_g^-$ ,  $^2\Delta_g$ , and  $^4\Sigma_g^-$  states. Only the  $^4\Sigma_g^-$  state can be treated within the single determinantal framework and is found to be bound by 0.66 eV; the other states are not expected, from Hund's rules, to be as stable as the  $^4\Sigma_g^-$  state.

In summary, we have found a total of five stable negative ion states of linear  $\text{Be}_3$ , whereas  $\text{Be}_3^-$  apparently possesses only one stable state—the  $^2\Sigma_g^-$  ground state. There is also reason to believe that some of the Feshbach-like negative ion states of linear  $\text{Be}_3$  which we were unable to treat within the single determinantal framework may also be stable. The stabilities of the  $^4\Pi_g$ ,  $^2\Sigma_g$ , and  $^4\Sigma_g^-$  states quoted above do not include any estimate of the correlation energy corrections. Because the quartet Feshbach-like states involve the "unpairing" of an electron, their correlation energies may be considerably ( $\sim 0.5$  eV) less than that of the neutral. Thus, in these cases, our predictions may overestimate the anion stabilities by as much as  $\sim 0.5$  eV.

The equilateral triangular geometry of neutral  $\text{Be}_3$  was found to possess a minimum-energy configuration with bond lengths of 4.32 a.u. which, according to our calculations, is stable with respect to dissociation by 0.06 eV. However, as we note later in connections with our calculation on  $\text{Be}_4$ , the errors in our predicted dissociation energies are probably of the order of 0.07 eV per Be atom. Thus, we are in no position to defend this claim that triangular  $\text{Be}_3$  may be stable.

As for the linear structure, both sigma and pi states of triangular  $\text{Be}_3^-$  were found to be stable with respect to electron detachment. The  $^2A_1'$  (sigma) state of  $\text{Be}_3^-$  is stable by 1.08 eV at an equilibrium bond length of 4.75 a.u., whereas the  $^2A_2''$  (pi) state has an equilibrium geometry of  $R = 4.11$  a.u. at which it is stable by 0.59 eV. Not surprisingly, the anions of triangular  $\text{Be}_3$  are more stable than the corresponding anions of linear  $\text{Be}_3$ . In fact, the RHF calculation on triangular  $\text{Be}_3$  at  $R = 4.32$  a.u. gives orbital energies of  $-0.09$  and  $-0.05$  eV for the  $3a_1'$  and  $1a_2'$  virtual orbitals, respectively.

In Fig. 4 we show the SCF potential curves for the neutral and anionic linear and triangular  $\text{Be}_3$  molecules. The energy of the  $^2A_1'$  state of equilateral  $\text{Be}_3^-$  is chosen as the reference energy, i.e., the zero of energy. The sigma and pi anion states of the triangular species are

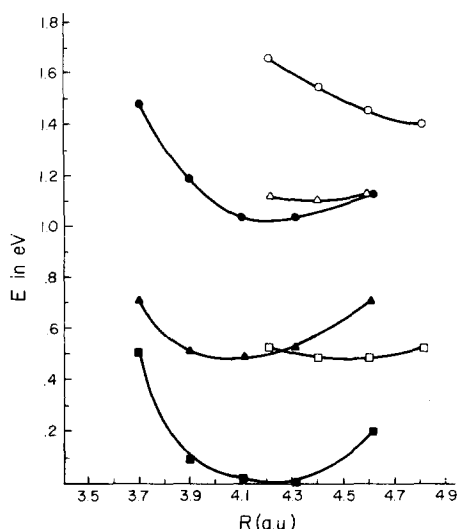


FIG. 4. Potential energy curves of linear and equilateral Be<sub>3</sub> and Be<sub>3</sub><sup>-</sup>. Equilateral Be<sub>3</sub>: ground state neutral (■), <sup>2</sup>A<sub>1</sub>' anion (▲), <sup>2</sup>A<sub>2</sub>' anion (●). Linear Be<sub>3</sub>: ground state neutral (□), <sup>2</sup>Σ anion (Δ), <sup>2</sup>Π anion (○).

seen to have equilibrium bond lengths which are approximately 0.3 a. u. shorter than those of the corresponding states of linear Be<sub>3</sub>. Although not enough points have been obtained for these six potential curves to permit accurate calculations of vibrational frequencies, it is clear that the force constants ( $\sim 7 \times 10^4$  dyne/cm) correspond to rather low vibrational frequencies. As mentioned above, our RHF calculations indicate that the  $X^1\Sigma_g$  state of linear Be<sub>3</sub> is repulsive over the range of internuclear distances studied here, while the ground state of triangular Be<sub>3</sub> is weakly bound. Actually symmetric linear Be<sub>3</sub> should have a van der Waals minimum of roughly 1–2 kcal (Dykstra *et al.*<sup>2(c)</sup> concluded that 0.7 kcal is a reasonable estimate for the van der Waals binding of Be<sub>2</sub>). We estimate that this minimum occurs for a bond length of approximately 5.0 a. u.

The lowest energy doublet pi and sigma anions of both forms of Be<sub>3</sub> have shorter bond lengths than the corresponding neutral species as would be expected for the addition of an electron to a strongly bonding orbital. We have not carried out calculations over a sufficiently wide range of bond lengths to find either the crossing points of the neutral and anion curves or the internuclear separations at which the pi and sigma anion states cross.

Nor have we investigated the possibility of the existence of Feshbach-type bound anions of triangular Be<sub>3</sub>, but we expect these states to be weakly bound or to lie somewhat above the ground state of the neutral (in this latter case, they would be resonances and, thus, would have finite lifetimes). Our main reason for expecting the Feshbach-type anions of triangular Be<sub>3</sub> to be less stable than those of the linear trimer is that the highest occupied molecular orbital (HOMO) of the triangular species is about 1 eV more strongly bound than is the HOMO of the linear Be<sub>3</sub>. Thus, the promotion of an electron from the antibonding HOMO to an unoccupied molecular orbital will be less favorable energetically than for the triplet species.

The atomic orbital coefficients of the  $2a_1'$ ,  $2e'$ ,  $3a_1'$ ,  $1a_2''$ , and  $3e'$  RHF orbitals of equilateral Be<sub>3</sub> are given in Table IV. The  $2a_1'$  and  $2e'$  MO's result primarily from the interaction of the Be 2s atomic orbitals; however, these MO's also contain an appreciable admixture of the atomic 2p functions. At a bond length of 4.32 a. u., the lowest unoccupied  $\sigma$  and  $\pi$  (i. e.,  $3a_1'$  and  $1a_2''$ ) orbitals of the neutral species are split by only 0.04 eV while in a UHF picture the  $^2A_1'$  and  $^2A_2''$  states are split by 0.53 eV. In Fig. 5 we plot the charge densities of the  $2a_1'$ ,  $2e'$ , and  $3a_1'$  RHF orbitals. The charge density plot of the  $2a_1'$  orbital is particularly interesting since it shows that much of the charge density of this orbital is "inside" the triangle.

#### D. Tetrahedral Be<sub>4</sub>

Due to the expense of the calculations for this cluster only one bond length was considered for the tetrahedron: 4.085 a. u. This value is the equilibrium bond length obtained by Brewington, Bender, and Schaefer<sup>2(b)</sup> from SCF calculations employing a 5s3p basis set. Our calculations predict this configuration of Be<sub>4</sub> to be stable with respect to dissociation by 1.86 eV, which is in reasonable agreement with the 1.55 and 1.74 eV SCF results of Brewington *et al.* using 5s3p and 4s2p1d basis sets, respectively. More recently, Dykstra, Schaefer, and Meyer,<sup>2(c)</sup> using a 5s2p basis set, obtained an SCF value of 1.47 eV for the dissociation energy. Using the same basis set, they carried out a calculation accounting for the dominant correlation effects and obtained a dissociation energy of 1.54 eV. From these results we can gain

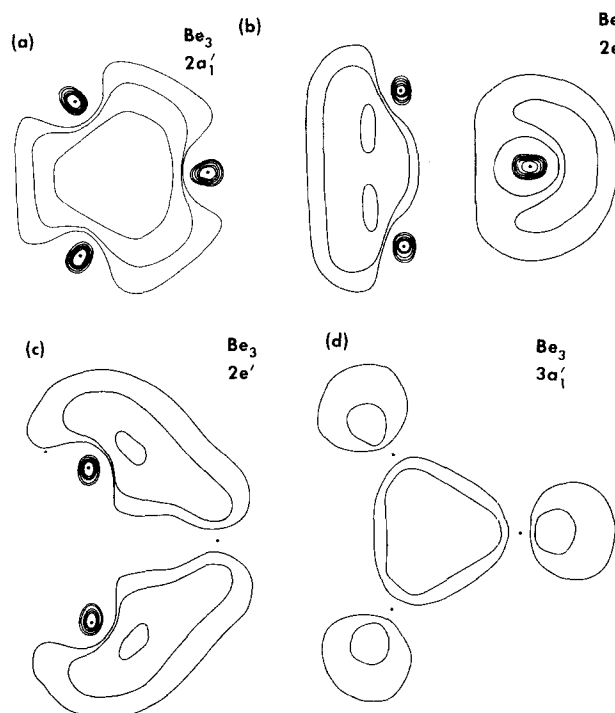


FIG. 5. Charge density maps of selected RHF molecular orbitals of equilateral Be<sub>3</sub>: (a)  $2a_1'$ , (b), (c)  $2e'$ , and (d)  $3a_1'$ . The contour lines  $|\psi(x, y, 0)|^2 = c$  are plotted for  $c = 0.0025, 0.0050, 0.010, 0.020, \text{ and } 0.040 e/a_0^3$ . The bond lengths are 4.32 a. u.

TABLE IV. Orbital energies and coefficients of the valence molecular orbitals of triangular Be<sub>3</sub>.<sup>a</sup>

Atomic /orbital function/energy (a.u.)	2a <sub>1</sub>	2e'	2e'	3a <sub>1</sub>	1a <sub>2</sub> ''	3e'	3e'
1s <sup>b</sup>	-0.132	0.078	-0.135	-0.004	...	0.023	0.040
1s'	-0.076	0.047	-0.081	-0.005	...	0.014	0.024
1s''	0.271	-0.146	0.253	0.008	...	-0.045	-0.079
1s'''	0.193	-0.257	0.446	-0.007	...	-0.056	-0.098
1s <sup>iv</sup>	0.017	-0.091	0.157	0.313	...	-0.521	-0.902
2p <sub>x</sub>	-0.099	0.094	0.065	0.201	...	-0.191	-0.069
2p <sub>y</sub>	0.057	0.173	0.094	-0.116	...	-0.152	0.019
2p <sub>z</sub>	...	...	...	...	0.197	...	...
2p' <sub>x</sub>	-0.004	0.065	0.008	0.232	...	-0.329	-0.064
2p' <sub>y</sub>	0.002	0.084	0.065	-0.134	...	-0.353	0.328
2p' <sub>z</sub>	...	...	...	...	0.287	...	...
1s <sup>b</sup>	-0.132	-0.156	...	-0.004	...	-0.046	...
1s'	-0.076	-0.093	...	-0.005	...	-0.028	...
1s''	0.271	0.292	...	0.008	...	0.091	...
1s'''	0.193	0.515	...	-0.007	...	0.113	...
1s <sup>iv</sup>	0.017	0.181	...	0.313	...	1.041	...
2p <sub>x</sub>	...	...	0.227	...	...	...	0.262
2p <sub>y</sub>	-0.114	0.011	...	0.232	...	0.179	...
2p <sub>z</sub>	...	...	...	...	0.197	...	...
2p' <sub>x</sub>	...	...	0.121	...	...	...	0.543
2p' <sub>y</sub>	-0.004	-0.028	...	0.267	...	0.216	...
2p' <sub>z</sub>	...	...	...	...	0.287	...	...

<sup>a</sup>The (x, y, z) coordinates of the three atoms are (2.1608, 0.0, 0.0), (-2.1608, 0.0, 0.0), and (0.0, 3.7427, 0.0) a.u.

<sup>b</sup>This set of functions is centered on the atom at (2.1608, 0.0, 0.0). The molecular orbital coefficients of the atom at (-2.1608, 0.0, 0.0) are determined by symmetry.

<sup>c</sup>This set of functions is centered on the atom (0.0, 3.7427, 0.0). We give the molecular orbital coefficients of this atom since the full D<sub>3h</sub> symmetry was not used in performing the calculations.

some feeling for the effects of basis set size and electron correlation on the stability of the cluster.

We obtained a  $\Delta$ SCF-level EA of 1.0 eV for Be<sub>4</sub> at a bond length of 4.085 a.u. This ion was formed by the addition of the "extra" electron to the LUMO (i.e., the 3a<sub>1</sub> orbital). Because this a<sub>1</sub> orbital is of bonding character, we expect that the bond length of the anion is 0.1–0.2 a.u. shorter than that of the neutral and that the adiabatic EA of Be<sub>4</sub> is 0.1–0.2 eV greater than the vertical EA. We did not explore the anion and neutral potential energy surfaces of Be<sub>4</sub> due to a lack of computer funds. We find there to be no bound  $\Pi$ -like state for tetrahedral Be<sub>4</sub> because the (e, t<sub>1</sub>, and t<sub>2</sub>)  $\pi$ -like orbitals are composed of 2p basis functions on the four Be atoms, directed perpendicular to lines from the center of the tetrahedron to the corner, which are not able to overlap effectively with one another.

There are several remarkable characteristics possessed by the tetrahedral Be<sub>4</sub> and Be<sub>4</sub><sup>-</sup> species. First, as was noted by Schaefer *et al.*,<sup>2</sup> the bonding in Be<sub>4</sub> is very

different from that in Be<sub>2</sub> and Be<sub>3</sub>: The binding energy for Be<sub>4</sub> is about 0.46 eV per atom while for Be<sub>2</sub> and Be<sub>3</sub> it is apparently less than 0.02 eV per atom. The reason for the relatively strong bonding of Be<sub>4</sub> may be understood from the examination of the valence molecular orbitals which are given in Table V. The a<sub>1</sub> and t<sub>2</sub> occupied valence orbitals have a significantly greater contribution from the atomic p orbitals than the occupied valence orbitals of Be<sub>2</sub> and Be<sub>3</sub>. This contribution from the p orbitals effects a substantially shorter equilibrium bond length for the tetrahedral Be<sub>4</sub>.

The anion of Be<sub>4</sub> is bound by 0.37 eV in the (RHF) Koopmans' theorem approximation at R = 3.941 a.u.; this stability is considerably greater than that arising in Be<sub>2</sub> or Be<sub>3</sub>. Whereas both forms of Be<sub>3</sub> possess two (one sigma and one pi) low-lying strongly bonding orbitals, only the first unoccupied orbital of Be<sub>4</sub> is strongly bonding. The e, t<sub>1</sub>, and t<sub>2</sub> unoccupied molecular orbitals, which are the  $\pi$ -like tetrahedral orbitals discussed earlier, are essentially nonbonding because of their inability



TABLE V. Orbital energies and coefficients of the valence molecular orbitals of tetrahedral Be<sub>4</sub>.<sup>a</sup>

Atomic orbital function/energy (a.u.)	2a <sub>1</sub>	2t <sub>2</sub>	2t <sub>2</sub>	2t <sub>2</sub>	3a <sub>1</sub>	3t <sub>2</sub>	3t <sub>2</sub>	3t <sub>2</sub>
	-0.557	-0.274	-0.274	-0.274	-0.014	0.041	0.041	0.041
1s <sup>b</sup>	-0.125	-0.084	0.119	...	0.001	0.024	0.034	...
1s'	-0.065	-0.055	0.077	...	0.001	0.010	0.014	...
1s''	0.225	0.168	-0.238	...	0.025	-0.012	-0.017	...
1s'''	0.116	0.249	-0.352	...	-0.031	-0.218	-0.308	...
1s <sup>iv</sup>	0.114	0.058	-0.083	...	-0.240	-1.789	-2.532	...
2p <sub>x</sub>	0.091	0.127	0.048	...	0.162	0.155	0.075	...
2p <sub>y</sub>	-0.064	0.138	0.127	...	-0.115	0.034	-0.155	...
2p <sub>z</sub>	...	...	...	0.227	...	...	...	0.143
2p' <sub>x</sub>	0.003	0.069	0.001	...	0.130	0.088	-0.358	...
2p' <sub>y</sub>	0.002	0.050	0.070	...	-0.092	0.424	-0.088	...
2p' <sub>z</sub>	...	...	...	0.099	...	...	...	0.486
1s <sup>c</sup>	-0.125	0.084	...	-0.119	0.001	-0.024	...	0.034
1s'	-0.065	0.055	...	-0.077	0.001	-0.010	...	0.014
1s''	0.225	0.168	...	0.238	0.025	0.012	...	-0.017
1s'''	0.116	0.249	...	0.352	-0.031	0.218	...	-0.308
1s <sup>iv</sup>	0.114	0.058	...	0.083	-0.240	1.789	...	-2.532
2p <sub>x</sub>	...	...	0.227	...	...	...	-0.143	...
2p <sub>y</sub>	0.064	0.138	...	0.127	0.115	0.034	...	0.155
2p <sub>z</sub>	-0.091	0.127	...	0.048	-0.162	0.155	...	-0.075
2p' <sub>x</sub>	...	...	0.099	...	...	...	-0.486	...
2p' <sub>y</sub>	0.002	0.050	...	0.070	0.092	0.424	...	0.088
2p' <sub>z</sub>	-0.003	0.069	...	0.001	-0.130	0.088	...	0.358

<sup>a</sup>The coordinates of the four Be atoms are (-1.97, 1.393, 0.0), (1.97, 1.393, 0.0), (0.0, -1.393, 1.97), and (0.0, -1.393, -1.97) a.u.

<sup>b</sup>This set of functions is centered on the atom at (-1.97, 1.393, 0.0). The molecular orbital coefficients for the atom at (1.97, 1.393, 0.0) are given by symmetry.

<sup>c</sup>This set of functions is centered on the atom at (0.0, -1.393, 1.97). The molecular orbital coefficients for the atom at (0.0, -1.393, -1.97) are given by symmetry. This second set of functions is included in the table since the full tetrahedral symmetry was not employed in the calculations.

ity to overlap effectively. Because the 2t<sub>2</sub> HOMO of Be<sub>4</sub> is ~2 eV more stable than the 4σ<sub>g</sub> HOMO of linear Be<sub>3</sub>, it is unlikely that Feshbach-like anions, in which an electron is promoted from this 2t<sub>2</sub> orbital, will be stable.

Therefore, tetrahedral Be<sub>4</sub> probably possesses only one stable anion. On the other hand, both the linear and square configurations of Be<sub>4</sub> should possess stable sigma and pi anions. However, these structures of neutral Be<sub>4</sub> are likely to be less stable (by over 1 eV) than the tetrahedral structure. Thus, it would probably not be feasible to form linear or square Be<sub>4</sub><sup>-</sup> "directly." Judging from our experience with Be<sub>2</sub> and Be<sub>3</sub>, we expect ΔSCF EA's of about 1.0–1.7 eV for the linear and square Be<sub>4</sub>. Thus, although the EA's of the linear and square Be<sub>4</sub> may be greater than that of tetrahedral Be<sub>4</sub>, the tetrahedral form of the anion is expected to be most stable.

The 3a<sub>1</sub>' and 2t<sub>2</sub> valence orbitals of tetrahedral Be<sub>4</sub> are plotted in Fig. 6. The plot of the LUMO is particularly interesting since it shows that the s and p atomic orbitals have hybridized such that much of the LUMO's charge

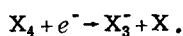
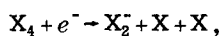
density is localized in the interior of the tetrahedron, thus making the 3a<sub>1</sub>' LUMO a rather strongly bonding orbital.

### III. DISCUSSION AND COMMENTS

In this paper we have presented the results of *ab initio* SCF calculations on the EA's of Be<sub>2</sub>, Be<sub>3</sub>, and Be<sub>4</sub> (see Fig. 7). While Be<sup>-</sup> is not stable, it appears that all the (Be)<sub>n</sub> clusters with n > 2 will possess stable anions. As the cluster size grows, the EA and IP should approach the work function of the bulk metal. The clusters considered are, of course, far too small to give EA's close to the work function<sup>23</sup> (3.92 eV), which was by no means the intent of this work.

The EA's of atomic Mg, Cd, Zn, and Hg, which also have an ns<sup>2</sup>np<sup>0</sup> valence configuration, have been experimentally determined<sup>15</sup> and all fall between -0.15 and -0.50 eV. Because of the presence of low-lying "empty" p orbitals in all of these atoms, we expect that all of the clusters X<sub>n</sub>Y<sub>m</sub> where X, Y = Be, Mg, Cd, Zn, or Hg

and  $n + m \geq 2$  will also possess stable anions. None of these cluster anions have yet been detected experimentally (nor have they been searched for, to the best of our knowledge). Due to the toxicity of Be and many of its compounds, it is likely that the first experimental studies will be carried on anions of Mg clusters. The smallest such cluster,  $\text{Mg}_2$ , is known<sup>24</sup> to be bound (i. e., to support vibrational levels) by  $\sim 1.2$  kcal. Because the  $\text{X}^-$  ions are not bound and the  $\text{XY}$  species are only weakly bound, the most direct methods of preparation of the  $\text{XY}^-$  ions are not likely to succeed. However, it may be possible, by nozzle expansion or related techniques, to obtain an appreciable concentration of  $\text{X}_4$  clusters. Low energy electron impact could then be used to attempt to prepare  $\text{X}_2^-$  or  $\text{X}_3^-$ :



The resulting ions could then be studied by photodetachment. For those species  $\text{X}_n\text{Y}_m$  which are stable it may be possible by near-resonant charge exchange with electronically excited Cs atoms, to directly form  $\text{X}_n\text{Y}_m^-$ . There is also a possibility that small clusters  $\text{X}_n$  could be formed by depositing X and Ar on a cold surface to form matrix isolated  $\text{X}_n$ . A strong reducing agent (e. g., Na) could then be used as a source of electrons to attach to the isolated clusters.

In future papers in this series we intend to present the results of calculations of the properties of  $\text{Be}_5$  and  $\text{Be}_6$  as well as their ions. It is possible that the trigonal bipyramidal structure of  $\text{Be}_5$  could form a stable dianion; we plan to carefully examine this possibility. Also, we intend to determine the contribution of electron correlation to the IP's and EA's as a function of cluster size. Whereas the calculations discussed in the present study

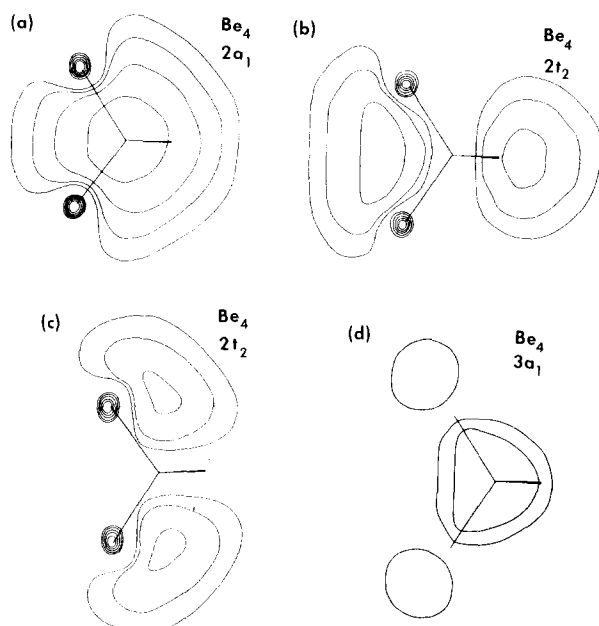


FIG. 6. Charge density maps of the  $2a_1$  and  $2t_2$  molecular orbitals of tetrahedral  $\text{Be}_4$  are plotted. The contour lines  $|\psi(x, y, 0)|^2 = c$  are given for  $c = 0.0025, 0.0050, 0.010, 0.020,$  and  $0.040 e/a_0^3$ . The bond lengths are 4.085 a. u.

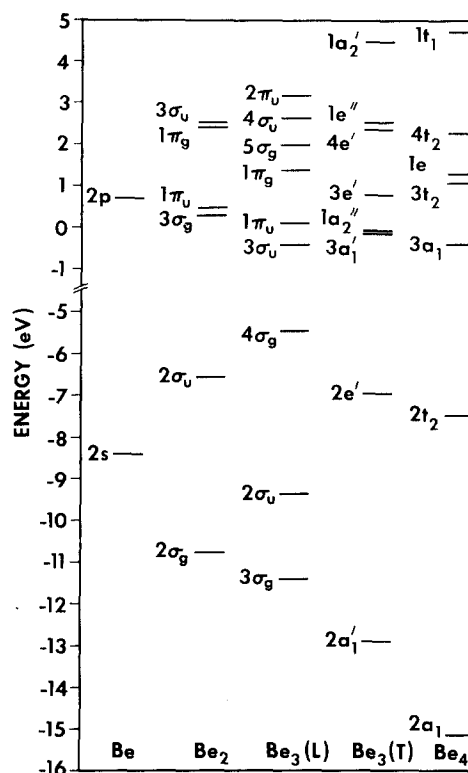


FIG. 7. Orbital correlation diagram for  $\text{Be}_1$ ,  $\text{Be}_2$ ,  $\text{Be}_3$  (linear and triangular), and  $\text{Be}_4$ . The orbital energies are obtained from our SCF calculations on the neutral molecules with the bond lengths 4.62 a. u. for  $\text{Be}_2$ , 4.62 a. u. for linear (symmetric)  $\text{Be}_3$ , 4.32 a. u. for equilateral  $\text{Be}_3$ , and 3.94 a. u. for tetrahedral  $\text{Be}_4$ .

were fully *ab initio*, we plan to repeat the calculations treating only the valence electrons and using pseudopotentials to incorporate the effects of the  $(1s)^2$  core electrons of Be. Similarly, full *ab initio* calculations as well as pseudopotential calculations will be performed on  $\text{BeMg}$ ,  $\text{Be}_2\text{Mg}$ ,  $\text{Mg}_2$ , and  $\text{Mg}_3$ . In the event that good agreement between the all-electron and pseudopotential valence-electron-only calculations is attained, we could then confidently use the pseudopotential approach to extend our calculations to larger clusters of Be and Mg as well as to Zn and Cd clusters, and mixed (alloy) clusters. This would then bring us much closer to systems which are of catalytic relevance.

From the knowledge of the IP's and EA's of the clusters it should be possible to make useful statements concerning the interaction of various adsorbates with the aggregates. In particular, from the IP's and EA's of the aggregates we can calculate electronegativities which, coupled with knowledge of an adsorbate's EA and IP (and hence its electronegativity), will allow the prediction of whether there will be a net gain or loss of electrons by the aggregate when it is involved in chemisorption of an atom or molecule.

Ideally, one would like to extend these *ab initio* calculations to clusters as large as 20–30 atoms. Such studies would yield important information concerning accumulation or depletion of electron density at "dangling" atoms or edges of the aggregates. Although *ab initio* calcula-

tions on clusters of this size are now feasible for species such as Li, Be, B, and C, they would be extremely expensive even if pseudopotential methods are employed. On the other hand, semiempirical and empirical calculations on rather large clusters can be carried out relatively inexpensively. Unfortunately, these procedures, as they are usually parameterized, do not yield accurate EA's because nowhere in the parameterization, which is essentially an implicit basis choice, is the diffuse nature of the anion incorporated. Thus, one of the important roles of detailed *ab initio* calculations on the small clusters is to permit the determination of new parameters to be used in the empirical and semiempirical methods, which then can be employed with some confidence to treat the larger anion systems.

*Note added in proof:* In recent SCF studies of  $Mg_2$  and  $Mg_2^-$  employing basis sets as large as  $8s5p1d$  we have been unable to find evidence for a stable  $Mg_2^-$  anion. [K. D. Jordan, G. Purvis, and J. Simons (unpublished results)]. This finding is most surprising in view of the  $Be_2/Be_2^-$  results presented in the present paper.

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stitute of Physics, Report 74-29, December 1974) to generate the integrals over Gaussian functions and the GRNFNC program to solve the Hartree-Fock equations. The GRNFNC program was developed by G. Purvis at the University of Florida's Quantum Theory Project.

- <sup>7</sup>We adopt the convention that the correlation energy in the case of an ion corresponds to the energy difference between the ion's UHF energy and its exact nonrelativistic energy. Of course, if we were to define the correlation energy relative to the ion's RHF energy, then the use of a UHF procedure includes part of the electron correlation. In any case, for the systems studied here the electron correlation—regardless of the definition adopted—is expected to be greater in the anion than the corresponding neutral.
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