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Path integral study of the correlated electronic states of Na$_4$–Na$_6$

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Feynman's path integral formulation of quantum mechanics is used to study the correlated electronic states of Na$_4$–Na$_6$. Two types of simulations are performed: in the first, the nuclei are allowed to move at finite temperature in order to find the most stable geometries. In agreement with previous calculations, we find that planar structures are the most stable and that there is significant vibrational amplitude at finite temperatures, indicating that the Born–Oppenheimer surface is relatively flat. In the second type of simulation, the nuclei are held fixed at symmetric and asymmetric geometries and the correlated electron density is found. Our results show that the electrons are localized, rather than delocalized as previous workers have concluded from examination of the single-particle orbitals. We find that the best picture of these clusters is that they contain three-center, two-electron bonds.

I. INTRODUCTION

The study of alkali metal clusters has intrigued chemists and physicists for a long time.[1] The evolution as a function of cluster size of the electronic states from localized to delocalized in nature is thought to involve physics similar to the metal–insulator and Mott transitions.[2] Experimental work has suggested the existence of "magic" cluster sizes[3–6]; clusters that appear particularly stable as a function of the number of atoms in the cluster. The magic cluster sizes do not correspond to the expected sizes if geometric packing is the origin of the stability (such clusters are seen, for instance, in xenon and argon clusters[7]). Geometric packing would be important if the valence electrons were more or less localized to individual atoms or bonds. An alternative explanation for the stabilities, first suggested by Knight, Clemenger, de Heer, Saunders, Chou, and Cohen[6] and since expanded upon by several groups,[8] is based on the assumption that the electrons are delocalized over the entire cluster, behaving in much the same way as electrons in a metal. In this picture, the nuclei are replaced with a smeared-out charge distribution (the jellium model) and the electronic problem is solved self-consistently in the local-spin density (LSD) version of density functional theory. The result is a hydrogen-like problem, with the degeneracy of different *l* states split because the charge distribution is not a point charge. The filling of different electronic shells is assumed to be accompanied by extra stability of the cluster and, hence, to predict the magic cluster sizes. The model predicts some, but not all of the magic cluster sizes; this has led to intense interest in using more realistic approaches to probe the geometric and electronic structure of small clusters. Density functional[9,10] and quantum chemical[11–13] calculations have been carried out on Li, Na, and K clusters. The conclusions of these studies are that the clusters are planar for up to 5–6 atoms and that the electronic structure is delocalized, as suggested by the jellium model.

There are several features of the previous work that cause concern with the conclusions regarding the electronic structure. (1) Quantum chemists have noted[11–13] that cor-rectly including electron correlation (using a CI approach, for instance) is essential in obtaining a correct ordering of the energies of different geometric isomers. However, both the density functional and quantum chemical calculations have analyzed the electronic structure in terms of single particle orbitals determined with either the LSD or Hartree–Fock approximations. If correlation is an important aspect of the energy, then it is certainly an important aspect of the electronic structure and attempts to describe the electronic states in terms of single-particle orbitals can lead to misleading interpretations. To correctly understand the electronic structure, it is essential to obtain the correlated electron density. This is impossible with DFT and difficult with quantum chemistry. (2) Most of the previous calculations have used a finite basis set expansion. If the electrons are becoming delocalized, the electronic orbitals are undergoing *qualitative* changes and the ability of an atom-based expansion must be questioned. It is therefore important to use a complete set of states (such as the position representation) to describe the electronic states. (3) Previous work has demonstrated[14] that the Born–Oppenheimer electronic surfaces, on which the nuclei move, are relatively flat, indicating that even at low temperatures there must be significant vibrational motion. All examinations of the electronic structure have, however, been performed at the minimum on the potential energy surface and have thus ignored any changes in the qualitative nature of the electronic structure that can occur when the atoms vibrate. In a previous paper,[15] we have demonstrated that vibrations have a significant effect on the nature of the electronic states in Na$_3^+$ and Na$_3$; in particular, vibrations tend to *localize* the electron density and, hence, contradict the conclusions of the previous workers.

Thus, it is important to study alkali clusters using a method that is capable of (a) determining the correlated electronic structure, (b) using a complete set of states, and (c) allowing for finite temperature fluctuations. The path integral formulation of quantum mechanics provides such a technique. Until recently, it has been limited for technical reasons to problems where exchange was nonexistent or was

TABLE II. The average instantaneous bond lengths for Na$_4$ (see text for definition). n_1 and n_2 correspond to arbitrary labels of the atoms, lengths are given in atomic units, and the numbers in parentheses represent one standard deviation.

n_1	n_2	Length (a.u.)	n_1	n_2	Length (a.u.)
Na 4					
1	2	5.72 (0.02)	2	3	7.17 (0.07)
1	3	6.16 (0.02)	2	4	7.63 (0.07)
1	4	6.46 (0.02)	3	4	12.29 (0.06)

well, the triplet state of the sodium dimer, and two electrons in a harmonic well.

III. CALCULATIONS

In our calculations, we treat only the valence electrons and use the $l = 0$ pseudopotential of Preuss et al.[17] to describe the electron-Na$^+$ interaction. Use of only the $l = 0$ component does not seriously affect the $l \neq 0$ energies in the isolated atom,[18] so we feel it can be used with sufficient accuracy in the larger clusters. In treating 3-particle exchange terms, we have used a product of 2-particle exchange terms. In test calculations, we found that a more accurate representation of the 3-particle exchange (such as what we did for particles localized in a harmonic well[16]) had no effect on the properties of Na$_5$, hence, we did not include the more time-consuming 3-particle exchange term in our calculations. We performed two types of calculations, one at fixed positions of the nuclei (denoted "frozen" in this paper) and the other in which the nuclei were allowed to move (denoted as "mobile" in this paper) in the manner described in our previous paper.[15] Mobile simulations were performed with $\beta = 1000$ a.u. (~ 300 K) with $P = 1600$ on an IBM 3090 located at LSU and frozen simulations were performed with $\beta = 250$ a.u. (~ 1200 K) (at this temperature, excited electronic state effects were unimportant) with $P = 400$ on Vaxstation 3000's located in the Department of Chemistry. The individual beads were moved according to the algorithm of Ceperley and Pollock,[19] as implemented by Coker et al.,[20] moving 25 beads at a time. In addition to the energies, we determined the geometric structure in the mobile simulations by performing two averages: (1) the average length of each bond, which gives information about the average geometry and

(2) the average of the bond lengths, sorted by magnitude, which gives information about the instantaneous geometry; that is, the geometry typical of a vibrational fluctuation about the average structure. In the mobile calculations, the initial geometries were chosen by fitting the Na$_2$ interaction with a classical Morse potential and minimizing the geometry of the N-atom cluster with this classical two-body interaction. The resulting initial geometries were tetrahedral (Na$_4$), trigonal bypyramidal (Na$_5$), and distorted octahedral (Na$_6$). A very small number of Monte Carlo passes were required for the cluster geometry to evolve to the structures discussed in the next section (all planar).

IV. ENERGIES AND GEOMETRIES: RESULTS AND DISCUSSION

The mobile clusters were simulated for 1000-2000 Monte Carlo passes at $\beta = 1000$ a.u. The average structures are shown in Fig. 1 and the average bond lengths are given in Table I and, for Na$_4$, the average sorted bond lengths are given in Table II. In the figure, distances are rounded off to reflect the standard deviation and the numbers in parentheses are density functional[9] and quantum chemical results.[13] The geometries found in our simulations represent fluctu-

TABLE III. Energies of the mobile simulations. $\langle T \rangle$, $\langle V \rangle$, and $\langle E \rangle$ are, respectively, the average kinetic energy, the average potential energy, and the average total energy (this includes vibrational energy). Numbers are in atomic units, and the number in parentheses represent one standard deviation.

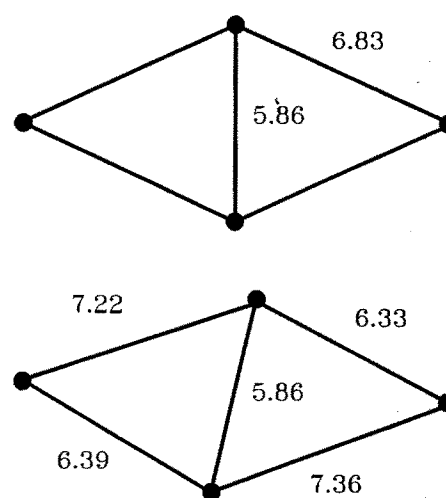| Cluster	$\langle E \rangle$	$\langle T \rangle$	$\langle V \rangle$
Na$_4$	$-0.8333(0.0014)$	$0.3286(0.0012)$	$-1.1619(0.0008)$
Na$_5$	$-1.0113(0.0017)$	$0.4247(0.0016)$	$-1.4360(0.0009)$
Na$_6$	$-1.2139(0.0022)$	$0.5128(0.0020)$	$-1.7267(0.0011)$

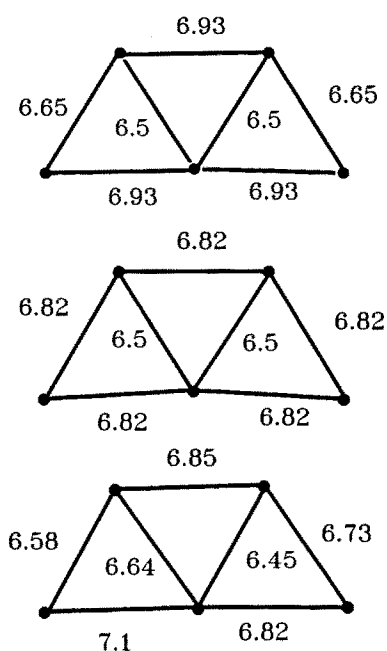FIG. 2. The two Na$_4$ isomers studied with frozen simulations. Units are atomic.

FIG. 3. The three Na_5 isomers studied with frozen simulations. Units are atomic.

TABLE IV. The energies of the frozen simulations. The clusters are listed in the order they appear in Figs. 2–4. Refer to Table III for explanation of $\langle E \rangle$, $\langle T \rangle$, and $\langle V \rangle$.

Cluster	$\langle E \rangle$	$\langle T \rangle$	$\langle V \rangle$
Na_4	— 0.8371(0.0025)	0.3272(0.0020)	— 1.1643(0.0011)
Na_4	— 0.8418(0.0030)	0.3287(0.0024)	— 1.1704(0.0012)
Na_5	— 1.0482(0.0024)	0.4185(0.0020)	— 1.4667(0.0009)
Na_5	— 1.0416(0.0022)	0.4240(0.0018)	— 1.4655(0.0009)
Na_5	— 1.0459(0.0022)	0.4196(0.0019)	— 1.4655(0.0009)
Na_6	— 1.2806(0.0027)	0.5021(0.0023)	— 1.7827(0.0009)
Na_6	— 1.2810(0.0031)	0.5145(0.0027)	— 1.7955(0.0011)

Energies of the three simulations are given in Table III and are in reasonable agreement with previous work, considering that vibrational energy is included in the energies.

As can be seen from Tables I and II, the fluctuations in the sorted bond averages are less than the fluctuations in the individual bonds, suggesting that the symmetric geometry that corresponds to the minimum on the potential energy surface is not the only geometry whose electronic structure should be studied. To investigate this further, we have performed frozen simulations at fixed nuclear geometries corresponding to symmetric and asymmetric configurations of the nuclei. The geometries and bond lengths are given in Figs. 2–4 where the differences in bond lengths between Fig. 1 and Figs. 2–4 are due to the desire to study precisely planar clusters. For Na_6, we studied two different "symmetric" geometries in order to assess the relative importance of symmetric distortions from a completely symmetric geometry. The energies of these calculations are given in Table IV. In accord with previous calculations, we find the potential energy surface to be very flat (the energies of the different geometries are the same to within statistical error). The atomization energies $E_b \equiv (E_n - nE_1)/n$ can be determined straightforwardly and are given in Table V, along with the results of previous calculations. In addition, we can calculate the energy stabilization with respect to various dissociation pathways. Our results are compared with previous calculations in Table VI.

Examination of the tables clearly shows agreement between our path integral work and the density functional and quantum chemical work (in some areas, we have obtained much better agreement with quantum chemical results than with density functional results). Overall, the present results support the conclusions of the previous workers with regard to energies and geometries. The main purpose of this paper, however, is to investigate the nature of the electronic structure of the sodium clusters; we shall find, in the next section, important differences from the conclusions of the previous studies.

ations about a planar geometry, as would be expected from previous results. The average geometries of the current work are in qualitative agreement with the previous calculations. It is clear from examination of the bond lengths that our finite temperature calculations show deviations from the symmetric geometries found in zero temperature calculations. Such deviations are due, of course, to the finite temperature vibrations that should be important in these clusters, particularly since the vibrational frequencies are so low.
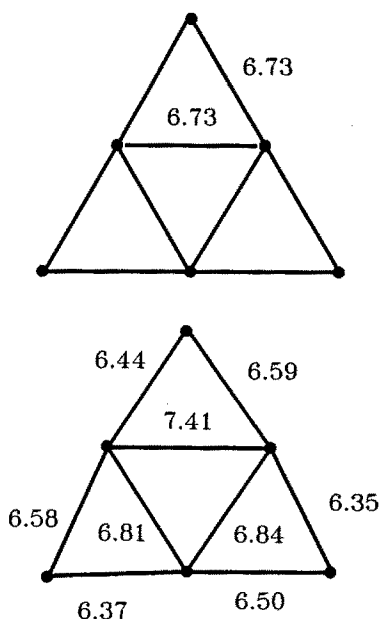

FIG. 4. The two Na_6 isomers studied with frozen simulations. Units are atomic.

V. CORRELATED ELECTRONIC STRUCTURE: RESULTS AND DISCUSSION

We have studied two aspects of the electronic structure. First, we looked at the difference in total electron densities of

TABLE V. Atomization energies per particle for the geometries shown in Figs. 2–4. E_{MC} are the current work, E_{DFT} are the results of Ref. 9, E_{SP} of Ref. 12, E^a_{KFK} and E^b_{KFK} of Ref. 13 for effective core and all-electron calculations, respectively. The units are eV and the numbers in parentheses represent one standard deviation.

	E_{MC}	E_{DFT}	E_{SP}	E^a_{KFK}	E^b_{KFK}
Na$_4$	0.478(0.029)	0.61	0.442	0.34	0.38
	0.510(0.032)				
Na$_5$	0.488(0.023)	0.64	0.472	0.36	0.41
	0.452(0.022)				
	0.476(0.022)				
Na$_6$	0.591(0.020)	0.73	0.545	0.42	0.47
	0.593(0.021)				

the symmetric and asymmetric geometries. Our previous work[15] on Na$_3$ and Na$_3^+$ indicated there were significant differences in electronic structure that accompanied relatively minor changes in geometry. These changes tended to localize electron density. Second, we have examined the correlated electron densities of the symmetric geometries by calculating the distribution of electron–electron distances for like-spin and unlike-spin electrons.

The difference in total electron densities between symmetric and asymmetric clusters is shown in Figs. 5–7 where solid lines correspond to regions with more electron density in the asymmetric geometry and dotted lines to regions with more electron density in the symmetric geometries. For reference, we give the total electron densities of the two geometries of Na$_4$ in Fig. 8. These difference plots suggest that the asymmetric geometries have electron density localized

between pairs of atoms near the edges of the clusters at the expense of electron density from the interior of the clusters. This is similar to the work of McAdon and Goddard,[11] who found a similar result for Li clusters (their work included a reasonable attempt to include correlation with the use of generalized valence bonds). Localization would be predicted if the electrons are rather weakly held and can adjust to the instantaneous positions of the nuclei by forming weak pair bonds between atoms that are relatively close. Thus, the effect of vibrations is to localize electron density.

A more useful way to examine the electron density is to calculate the distribution of electron–electron distances. The effects of correlation and (if present) localization should be apparent in these plots. Since it appears that the asymmetric structures have localized electron density, we have only examined the symmetric clusters' electron–electron distances.

TABLE VI. Fragmentation energies in eV. (MBC) denotes the results of Ref. 9, (SP) denotes the results of Ref. 12, and (KFK) denotes the results of Ref. 13. Numbers in parentheses represent one standard deviation and our results for Na$_3$ and Na$_2$ were obtained using our previous work (Ref. 15).

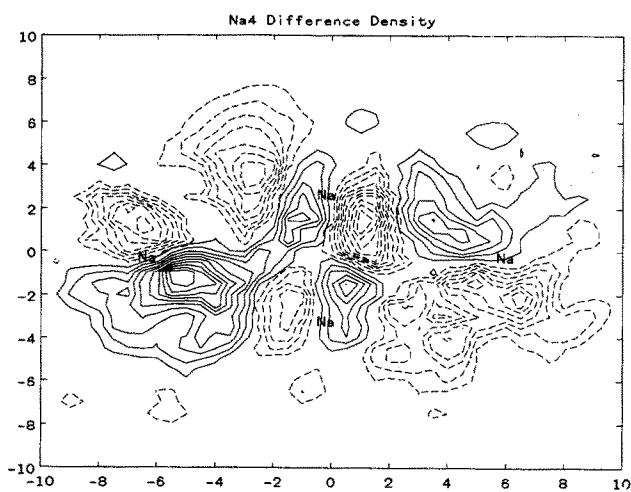| Parent/Fragment	Na/Na$_{n-1}$	Na$_2$/Na$_{n-2}$	Parent/Fragment Na$_3$/Na$_{n-3}$
Na$_2$	0.79 (0.05)		
	0.91 (MBC)		
	0.70 (SP)		
	0.57 (KFK)		
Na$_3$	0.34 (0.05)		
	0.40 (MBC)		
	0.25 (SP)		
	0.17 (KFK)		
Na$_4$	0.78 (0.07)	0.33 (0.09)	
	0.63 (MBC)		
	0.81 (SP)	0.36 (SP)	
	0.62 (KFK)	0.23 (KFK)	
Na$_5$	0.53 (0.09)	0.52 (0.08)	
	0.76 (MBC)		
	0.59 (SP)	0.71 (SP)	
	0.44 (KFK)	0.49 (KFK)	
Na$_6$	1.11 (0.10)	0.86 (0.11)	1.29 (0.08)
	1.03 (MBC)		
	0.94 (SP)	0.83 (SP)	1.39 (SP)
	0.72 (KFK)	0.79 (KFK)	1.03 (KFK)

FIG. 5. Na$_4$ difference density between the two isomers shown in Fig. 2. Solid (dotted) lines correspond to regions with more (less) density in the asymmetric isomer. The positions of the nuclei are indicated with symbols Na. Units are atomic.
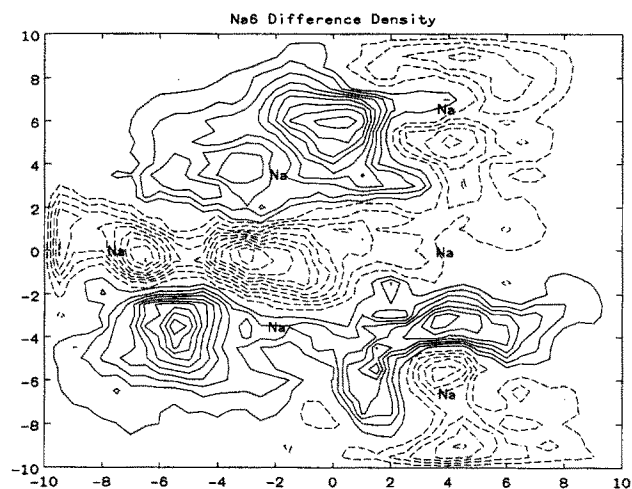

FIG. 7. Na$_6$ difference density between the two isomers shown in Fig. 4. Solid (dotted) lines correspond to regions with more (less) density in the asymmetric isomer. The positions of the nuclei are indicated with symbols Na. Units are atomic.

In Figs. 9–11, we have plotted the distribution of up–up, up–down, down–down, and down–up, distances for the symmetric clusters (here the first label indicates the tagged particle from which the distances are measured). In each case, we have sorted the distances by magnitude and give the distribution for each distance. Our results are best understood by examining the plots for Na$_4$ and Na$_6$. For each cluster, note that the peaks in the like-spin and unlike-spin distributions occur at the same distances, except for a peak at short distances occurring in the unlike-spin distributions. This suggests that electrons are occurring in pairs (and hence that

the peak at short distances in the unlike-spin distribution corresponds to the paired electron). Examination of the total electron density shown in Fig. 8 suggests that electrons are paired in the centers of triangles of Na atoms, forming weak 3-center, 2-electrons bonds. With this in mind, the Na$_5$ distribution can be understood in the same way, if a single up electron resides in the middle triangle of the cluster (in our simulations there were 3 up and 2 down electrons).

Thus, we are led to the conclusion that the electrons tend to spin pair in the interior of triangles, forming 3-center, 2-electron bonds. As a check on our interpretation of the distributions, we have assigned a "site" to the middle of each triangle of each cluster and calculated the fraction of configurations that had a certain set of electrons closest to a site.
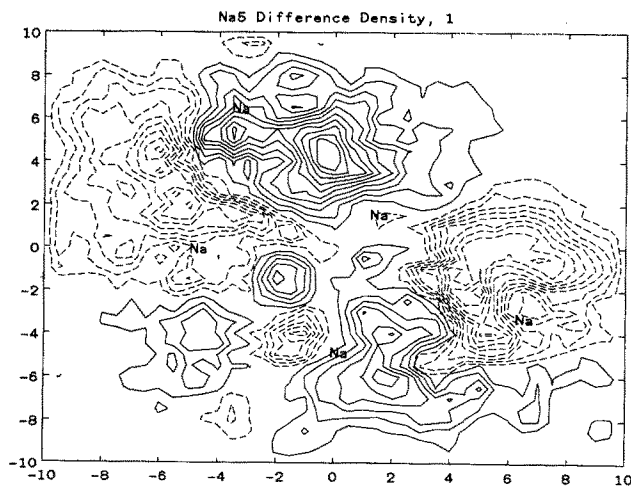

FIG. 6. Na$_5$ difference density between the bottom and top isomers shown in Fig. 3. Solid (dotted) lines correspond to regions with more (less) density in the asymmetric isomer. The positions of the nuclei are indicated with symbols Na. Units are atomic.
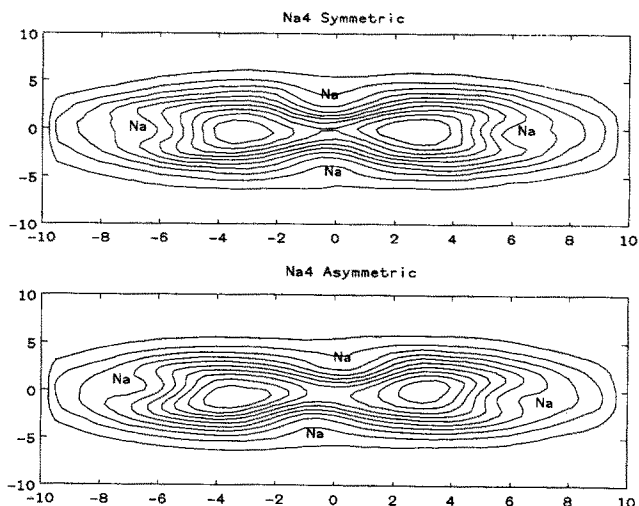

FIG. 8. Total electron densities for the symmetric and asymmetric isomers of Na$_4$ studied with frozen simulations. Units are atomic.
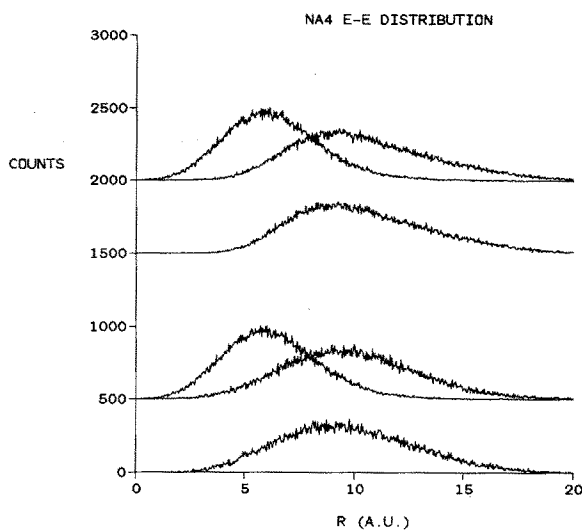
FIG. 9. Electron–electron distance distributions for Na$_4$-Na$_6$. From bottom to top, the plots are up–up, up–down, down–down, and down–up distributions where the first label indicates the tagged atom from which distances are measured. When there is more than one electron-tagged atom distance, the distances were sorted and are shown as individual traces. Units are atomic.

FIG. 11. See caption to Fig. 9.

The results are shown in Figs. 12–14, where the percentages are the total for all equivalent structures (that is, for Na$_4$, for example, there are two structures with three electrons in one triangle, each contributing 10%). A detailed examination of the configurations that have more than one like-spin electron per triangle 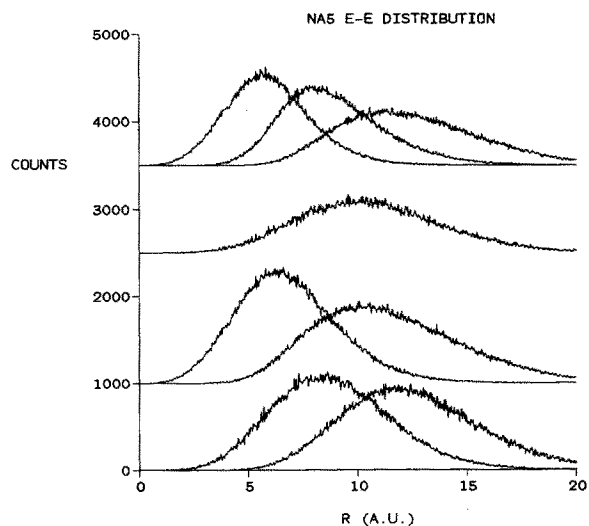indicates that there is still a large distance between such electrons and that the electrons are actually quite close to the edges of the triangles.
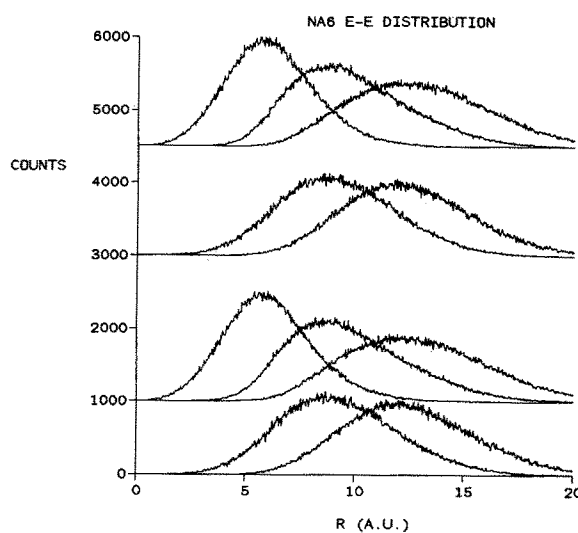
Thus, it is clear that our interpretation of the electron–electron distribution plots is substantially correct. It is important to note that while there is a dominant electron configuration for each cluster, there are other configurations that contribute nonnegligibly to the overall electronic structure. This is, perhaps, foreshadowing the onset of delocalized density that most workers invoke when explaining the stability of the clusters and may suggest why simple models such as jellium give some reasonable results.

VI. CONCLUSIONS

We have examined, for the first time, the correlated electron density of sodium clusters. By performing both "fro-

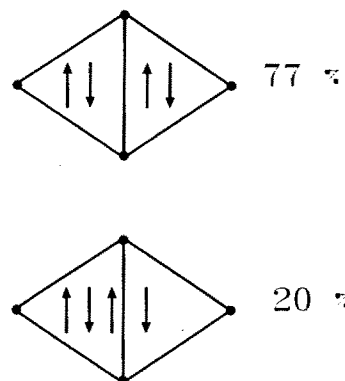FIG. 10. See caption to Fig. 9.

FIG. 12. Correlated electronic configurations determined from assigning a site to the middle of each triangle in the cluster. Percentages represent the fraction of all configurations studied that had a particular configuration.
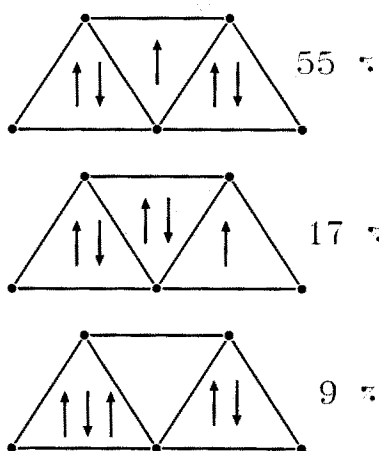
FIG. 13. See caption to Fig. 12.

zen" and "mobile" calculations, we have found the major effect of vibrations is to localize electron density between atoms. Our frozen calculations demonstrate substantial agreement between our work and previous work for those properties which we can compare (atomization energy, structure, and fragmentation energy). In contrast to the conclusions of previous studies, though, we find that 3-center, 2-electron bonds are a major part of the correlated electronic state. This suggests that it is incorrect to think of these clusters in terms of delocalized single electron pictures, which may give the correct result for energies (when correlation is included), but which give a misleading representation of the electronic states.

Thus, the planar geometries found in Na$_4$–Na$_6$ do not have delocalized electrons in the sense that previous workers have suggested. It is clear, though, that the electron density is not tightly bound and that larger clusters may indeed show significant delocalization. It will be interesting to examine clusters where deviations from planar geometries should occur. Such calculations are underway.
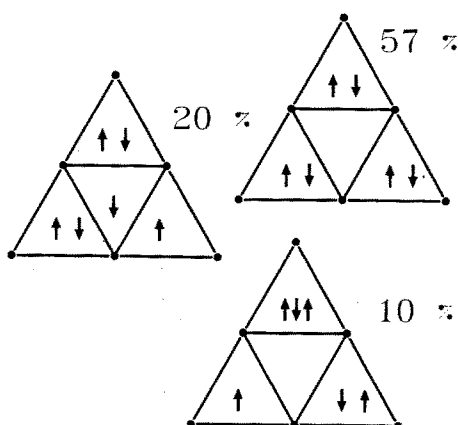
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FIG. 14. See caption to Fig. 12.

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