Localized-Orbital Hartree-Fock Description of Alkali-Metal Clusters

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We propose a new variational method, based on the *ab initio* Hartree-Fock methods, for the purpose of calculating efficiently both the equilibrium geometry and the stability of alkali-metal microclusters. Applying this method to lithium clusters, up to Li_{36}, we are able to find a close correlation between the observed magic numbers and the calculated stable cluster size. Furthermore, we find that lithium clusters larger than Li_{26} have an ordered structure while clusters smaller than this do not. This is suggestive of the evolution of the clusters to the bulk structure of solid lithium.

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The problem of how a cluster of atoms changes from a molecule to a solid with increasing the number of atoms has recently become an important subject in condensed-matter physics, and thus is now of enormous interest. During the past decade, with advances such as the development of noninteracting size-selected cluster beams,[1] it has become possible to study experimentally the physics of this problem. Many interesting phenomena have been observed. For example, Knight *et al.*[2] have found that clusters with "magic numbers" of atoms are particularly stable. Even, Ben-Horin, and Jortner[3] have shown that Kr clusters exhibit a nonrigid-to-rigid transition at the cluster size of $N=17$. In addition, electron microscopy measurements by Iijima and Ichihashi[4] have shown that, at some unknown cluster size, noble-metal clusters exhibit a crystal structure, and Rademann *et al.*[5] and others[3,6,7] have found a transition to the solid for Hg and Kr clusters when the clusters exceed several dozen atoms. Because of the difficulties in the computational techniques, however, theoretical investigations into microclusters have only begun very recently,[8] and their properties are still far from being understood. Many of the *ab initio* numerical techniques, such as self-consistent-field (SCF) Hartree-Fock (HF) methods and configuration-interaction methods, require enormous computer resources even for comparatively small clusters, and the modeling of the transition of clusters from a molecule to a solid has not been possible.[9] Other techniques, in particular, first-principles molecular-dynamics methods,[10] are able to deal with a larger number of atoms.[8,11] These techniques, however, rely on the local-density approximation, and it is not certain at the moment whether this is valid for very small systems due to the self-interaction problem.[12] In addition, the computation time required by these methods is prohibitively long, such that an extensive study of large clusters is not easy. Recently, however, cluster simulations have become popular in calculating bulk structural and electronic properties, and it is all the more important to develop a clear theoretical understanding of the transition of a cluster into a solid.

Here we present the details of a method which has been developed with this in mind. It is based on the *ab initio* Hartree-Fock methods, and makes use of the shape of the electron wave functions in a cluster to minimize the number of orbitals while maintaining the correct local electron density. With this, systems much larger than currently possible with the usual *ab initio* Hartree-Fock 3ethods may be treated from first principles. We have applied it to Li_N clusters for N up to 36, where it has successfully reproduced the magic numbers, as well as given some new insight into the reasons for their stability. Our results also show that clusters larger than Li_{26} have an ordered structure while clusters smaller than this do not, suggestive of an evolution to the bulk structure of solid lithium.

The present method makes use of a feature of atomic clusters in that the electron density is localized at interstitial regions surrounded by three or more atoms (see Fig. 1). Such configurations, which we shall call "glue bonds," have been found in lithium clusters,[13,14] as well as in boron clusters.[15] They may be considered as localized orbitals (LO) similar to the conventional chemical bonds. In terms of these glue bonds, it is possible to explain qualitatively the stability and equilibrium geometry of a cluster.[13-15] For lithium clusters, self-consistent-field calculations show that they are approximately spherical in shape (Fig. 1) and are localized interstitially inside a triangle or a polygon. Our idea is to make use of the near-spherical geometry of the glue bonds, and approximate them by ellipsoidal Gaussian orbitals (EGO),

$$\phi_a(\mathbf{r})=\exp\left[-\sum_{i,j}^{x,y,z}\alpha_{ij}^{a}(r_i-R_i^a)(r_j-R_j^a)\right], \tag{1}$$

where R_i^a represents the ith ($i=x,y,z$) component of the position $\mathbf{R}^a$ at which the amplitude of the ath LO takes a maximum value, and α_{ij}^{a} represents the exponent of the ath LO. The EGO's are then orthonormalized to form a single Slater determinant, which corresponds to a many-body wave function of a cluster. An SCF Hartree-Fock approach is then used to evaluate the total energy of the cluster. The positions of the atomic nuclei, $\mathbf{R}^a$, and the exponents α_{ij}^{a} of the EGO's are obtained variationally by minimizing the total energy. In doing so, the center of

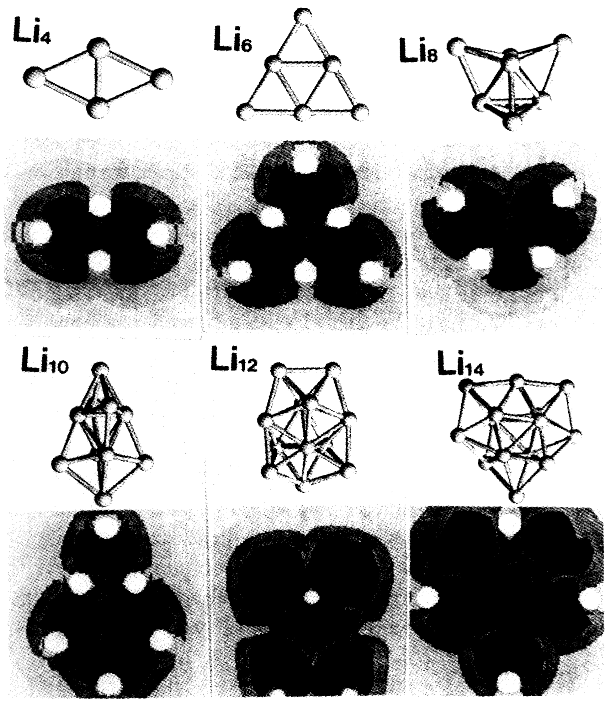

FIG. 1. The equilibrium geometries of lithium clusters Li_N with N ranging from 4 to 14, calculated by the SCF method (upper figure), and the LO's of the clusters (lower figure). The black regions correspond to the maximum amplitude of the LO's. Note that each black region correspond to one LO.

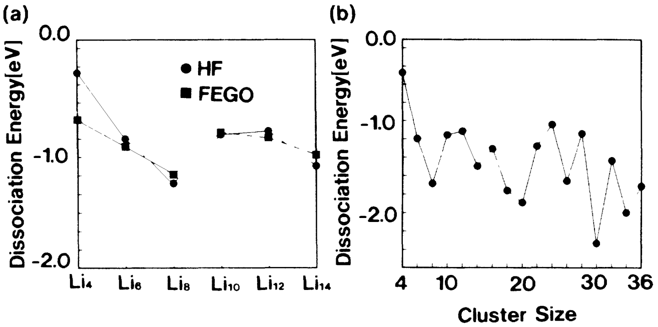

FIG. 2. (a) The dissociation energy for lithium clusters calculated by the FEGO method and by the SCF-HF method. (b) The dissociation energy for lithium clusters calculated using the FEGO method.

each EGO reaches an optimal position by "floating" in the cluster. In this context, the method is called the floating ellipsoidal Gaussian orbital (FEGO) method. This method has also been used for some covalent molecules.[16]

The computational advantage of the method lies in choosing the glue bonds to be represented by the EGO's. This is physically sensible, since they are roughly spherical, and the electron density may be well represented. The result is a reduction in the basis size, such that much larger systems may be tackled. We would like to add that this may be formulated rigorously[14] in terms of the Edmiston and Ruedenberg LO's,[17] which have been associated with the orbitals involved in chemical bonding, electron lone pairs, and inner atomic shells.[17] Full details of this will be published elsewhere.[18]

For further computational efficiency, we have used norm-conserving pseudopotentials.[19] With this, the number of basis functions can be further reduced. The overall increase in computational efficiency means that the optimization procedure may be carried out for many different initial geometries. This is particularly important for large clusters for which many metastable geometries exist.

We have applied this method and calculated the equilibrium geometry and the total energy of neutral lithium clusters, consisting of an even number of atoms, Li_N with N from 2 to 36.

We first compare the FEGO results with those calculated by the SCF method, at least up to Li_{14}. For larger clusters the SCF method could no longer be used because of computational limitations. The topology of the most stable equilibrium geometry is reproduced well by the FEGO. The interatomic distances are smaller by 2%, on average, than those obtained by the SCF method. The dissociation energy $\Delta = E_N - E_{N-2} - E_2$ is also well reproduced [Fig. 2(a)].

For the larger clusters, the dissociation-energy curve [Fig. 2(b)] shows minima at $N=8$, 14, 18, 20, 26, 30, and 34, corresponding to the "magic numbers" for stable clusters, while it has maxima at $N=10$, 12, 16, 22, 24, 28, and 32. This behavior is very similar to the dependence on the cluster size of the mass spectra data on Na observed by Knight *et al.*[2]

The optimized cluster geometry is highly complicated, and the full details will be published elsewhere. However, the basic properties may be characterized by the radial distribution function (RDF) and the bond-angle distribution function (BDF), as shown in Fig. 3. The RDF shows a general feature for all clusters, consisting of two main peaks and a gap in between them. The first peak appears at $R \simeq 6$ bohrs, which corresponds to the first-nearest-neighbor distance. A second peak may be seen at $R \simeq 10$ bohrs. However, its broad width suggests that the second-nearest-neighbor distance may only be defined weakly for the cluster sizes considered. The BDF shows, similarly, two peaks at 60° and 120°, characterizing the local network of the atomic positions, and in support of the idea that the atoms in Li clusters form regular triangular or tetrahedral networks.[9] Above all, we emphasize that for both radial and bond-angle distribution functions the distribution between the two peaks is almost zero for $N \geq 26$, contrary to the case for the smaller clusters. This shows that there is a distinct qualitative difference between the geometry of the smaller clusters and the larger ones, and suggests that, for Li_N

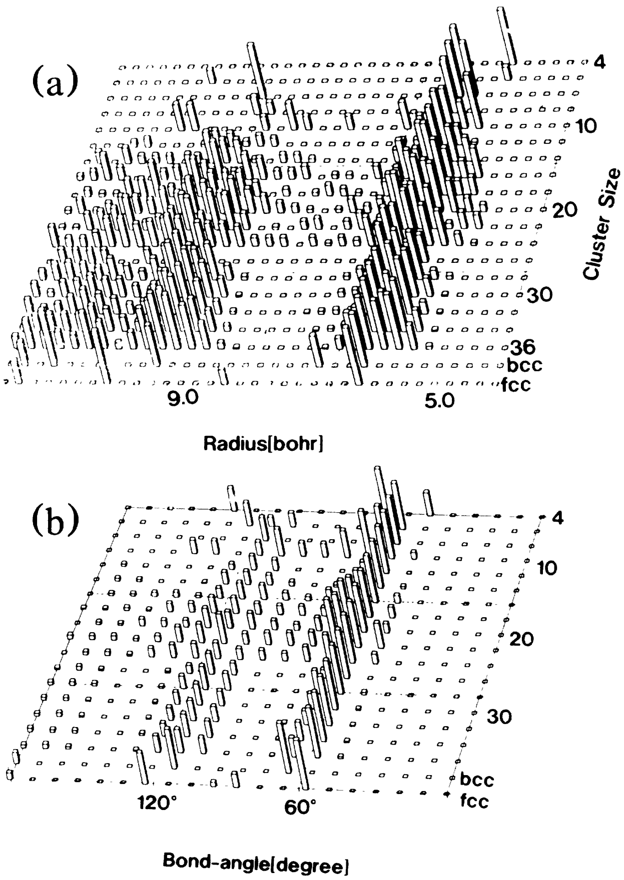

FIG. 3. (a) Radial distribution functions and (b) bond-angle distribution functions for Li_N clusters with $N=4$ to 36 calculated by the FEGO method. The distribution functions of bcc and fcc clusters are also shown for comparison.

clusters, there is a structural change to a more ordered phase at $N=26$. It should be noted that neither the RDF nor the BDF for even the largest cluster corresponds to those of a bulk crystal (Fig. 3). This implies that the clusters do not take up the bulk ordering at this size.

In the rest of this Letter we shall interpret the above results using the concept of the glue bonds, and show that this can give us a new insight as to the reason for the structural stability. In general, the electrostatic energy of a cluster may be lowered by arranging the atoms in a compact geometry. The exchange energy, however, is lowered only if the atoms are arranged in a way favoring covalency. The interplay between these two factors determines the equilibrium geometry. In terms of the glue bonds, this balance may be understood as the lowering of the exchange energy owing to the formation of the glue bonds versus the increase in the electrostatic energy due to distorting away from a compact geometry. For example, for small lithium clusters, such as Li_4 and Li_6, the cluster geometry is flat, which is electrostatically unfavorable. However, the flat geometry is favored for the hybridization of the $2s$ and $2p$ orbitals of the lithium atoms to form the glue bonds (see Fig. 1). This reduces the exchange energy, which dominates.

For very large clusters, geometrical restriction becomes severe, especially for the inner cluster region, so that the distortions needed for the distinct formation of glue bonds may not be realized. The result is a well-defined, rigid geometry. In the intermediate size, both effects compete, leading to a variety of phenomena. Our results suggest that the critical size for a rigid, solidlike structure is 26 atoms for Li clusters, and the change is abrupt.

Next we consider the relation between the glue bonds and the stability of the cluster. From the above discussion we expect that a cluster will be stable when there is the distinct formation of the glue bonds, and the atomic arrangement is compact. Li_8 and Li_{26} are typical examples. They have three equivalent principal moments of inertia, that is, they have an isotropic geometry. At the same time, distinct glue bonds are formed. For Li_8 the glue bonds are arranged tetrahedrally (Fig. 1), and for Li_{26} they are arranged approximately icosahedrally. As expected, they are stable, as seen from their dissociation energy, Fig. 2(b). Although we are not able to explain all the stable clusters by this criterion, it is an important factor in accounting for their stability.

Finally, we would like to mention the origin of the glue bonds. We consider that the formation of the glue bonds is due to electron confinement effects. That is, since electrons are confined in a cluster, the wave function, or the charge density, consists of nodes and peaks, with the peaks corresponding to the glue bonds. Therefore, as the cluster size becomes larger, the glue bonds will become less well defined.

In summary, we have developed a new *ab initio* Hartree-Fock-type method, the FEGO method, in which the localized electron density of a cluster, or the glue bond, is represented by a floating ellipsoidal Gaussian orbital, and its position and width are determined by minimizing the total energy. Applying this method to lithium clusters, we have found that it is accurate compared to *ab initio* SCF methods. The calculated dissociation energies are found to correspond well with the measured mass spectrum of alkali-metal clusters. The calculated optimized geometries suggest that an evolution occurs at $N=26$ to a more ordered, but not bulklike, structure. We expect that this structural change may be observed with advances in experimental techniques.

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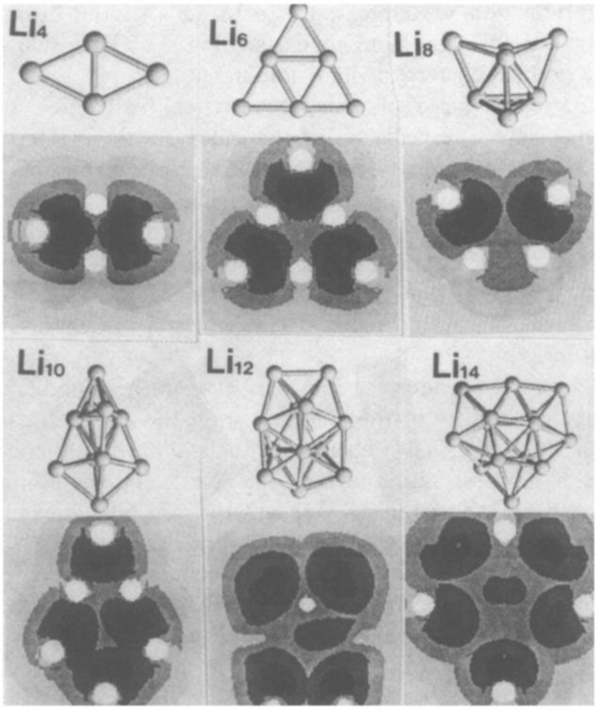

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