PHYSICAL REVIEW B VOLUME 43, NUMBER 11 15 APRIL 1991-I

Electronic structure of small clusters of Li and a Li-Mg compound

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(Received 23 April 1990; revised manuscript received 24 July 1990)

Local-density-functional (LDA) theory is employed to study the electronic structure of Li_9 and Li_{15} with body-centered-cubic geometry and Li_6Mg with simple-cubic geometry. The size of the basis set is found to be very important for a determination of the cluster properties. In a special subspace of basis functions, the cluster of Li_{15} can reproduce many properties of bulk lithium. The equilibrium lattice constant of Li_6Mg calculated is in excellent agreement with values obtained with other calculations, while results on the binding energy and ionization potential are somewhat different. For these a detailed discussion is made.

I. INTRODUCTION

In recent years local-density functional (LDA) theory has enjoyed much success in the study of electronic structure of clusters.[1-4] Clusters are often used as models in describing crystal and point defects.[1-8] Based on previous work,[1-4] we present in this paper the electronic structure of Li_9 and Li_{15} with body-centered-cubic geometry and Li_6Mg with simple-cubic geometry in the framework of local-density-functional theory. The primary aim of this paper is to study the relationship between finite-sized clusters and bulk metal. Usually, the choice of cluster size depends on the questions one wishes to address. If the cluster is just large enough to yield the bulk value of a property one wants to study, then, for that particular property, studying the cluster is equivalent to studying a bulk specimen. However, given a certain size of cluster, one can obtain different results, even for the same property. For example, the lattice constant of a cluster is found to be very different.[9] In fact, it is often discovered that the calculated properties of molecules and clusters are sometimes strongly dependent on the particular basis set used in the calculations. The question we now pose is that when we use the cluster as a model to describe properties of a solid, does there exist a special basis set in which a cluster can exhibit many bulk properties? To answer this question, we use different basis sets in this work to study the electronic properties of the clusters Li_9 and Li_{15}. We hope to shed some light on how well a cluster can represent a solid. For the study of an impurity in solid, we are interested in the behavior of Li_6Mg in the framework of LDA. We will present the results of Li_6Mg together with those of Li_9 and Li_{15} in the following sections.

II. METHOD

The method employed in these calculations has been described in detail in Refs. 1–4 and 10. Only the basis sets are given below. For the clusters of Li, the basis sets of 4*s* and 8*s* are those of the 2G and 4G from Mezey and Kari,[11] containing four *s*-like functions and eight *s*-like functions, respectively. The 8*s*1*p*, 8*s*2*p*, and 8*s*3*p* basis sets are based on the 4G, on which one, two, and three *p*-like functions with parameters of 0.145, 2.5, and 0.07 are added by the present author. The 9*s*4*p* basis set is that of Huzinaga,[12] containing nine *s*-like functions and four *p*-like functions. When one *d*-like function with a parameter of 1.008 is added to it by the present author, the 9*s*4*p*1*d* basis set is obtained. In the calculations for Li_6Mg, the basis set for Li atoms is the 9*s*4*p* described as above, and the basis set for the Mg atom is 12*s*6*p*1*d*, containing 12 *s*-like functions, six *p*-like functions, and one *d*-like function. The 12*s*6*p* are from Veillard.[13] The exponent of the *d*-like function is from Collins *et al.*[14]

III. RESULTS AND DISCUSSION

Our results are presented in this section, where they are compared with other calculations and experiment.

A. Li_9 and Li_{15}

The total energies of Li_9 and Li_{15} are calculated at several lattice spacings in the neighborhood of the minimum. After a least-squares fit to the total energies, we estimate the equilibrium lattice constants. The equilibrium lattice constant of Li_9 in all basis sets except the 4*s* one is smaller than the bulk value of 6.597 a.u. and decreases as the size of the basis set increases, ranging from 6.888 to 5.661 a.u. Li_{15} has the same trends but the value is larger than that of Li_9 in the same basis set. Thus we are given the possibility of choosing the basis set in the calculations so as to get the equilibrium lattice constant of a cluster as close to the bulk value as we want to. Fortunately, in such a basis set the cluster can reproduce many other properties of bulk better than in other basis sets. The best basis set is 8*s*1*p* in our calculations. The equilibrium lattice constant of Li_{15} is 6.4878 a.u. Certainly, a better basis set exists as discussed above. In Table I, we list the equilibrium lattice constant, conduction-band width, cohesive energy, energy gap, bulk modulus, and ionization potential of Li_9 and Li_{15} in the basis set of 8*s*1*p* as well as some experimental values for comparison.

TABLE I. Properties of ground state of Li_9 and Li_{15} is the basis set of $8s1p$. The equilibrium lattice constant (denoted by a_0) is given in bohrs. E_c is the cohesive energy, given in Ry. E_w, E_g, and IP are conduction-band width, energy gap, and ionization potential, respectively, in eV. B is the bulk modulus in 10^{10} dyn/cm^2.

Cluster	a_0	E_w	E_c	E_g	IP	B
Li_9	6.276	2.886	0.0675	43.15		7.0
Li_{15}	6.4878	2.739	0.0893	43.32	4.643	8.9
Expt.	6.597[a]	3.22[b]	1.22[a]			11.5[b]

[a] Reference 15 and references therein.

[b] Reference 7 and references therein.

The conduction-band width has the same trends as those of the equilibrium lattice constant. The value of Li_9 for this quantity ranges from 3.74 to 2.56 eV calculated at the bulk lattice constant, covering the experimental value of 3.22 eV (Ref. 7 and references therein) and the results of 3.47 eV from band calculation.[15] In the basis set of $8s1p$, the conduction-band width from Li_{15} at the equilibrium lattice constant is 2.74 eV, about 0.05 eV larger than that obtained at the bulk lattice constant. This implies that we can choose a better basis set to obtain the conduction-band width as close to the bulk value as possible without making other corrections in the theory.

The cohesive energy increases with increasing cluster size. But it increases for Li_9 and decreases for Li_{15} as the size of the basis set increases. In the basis set of $8s1p$, the cohesive energy of Li_{15} is 0.089 Ry per atom. Rao *et al.*[5] pointed out that it can refer to the surface effect. Following their procedure, we estimate the surface energy per atom of Li_{15} is about 0.033 Ry. When we add this correction to the cohesive energy of Li_{15}, our result is in very good agreement with experiment. If we use the total energy of a free Li atom from a non-spin-polarized calculation, in which the input charge density for spin-up and spin-down electrons is the same, the cohesive energy of Li_{15} in the present work is 0.108 Ry, which is 89% of the experimental value.

The bulk modulus B is defined as

$$B = v_0 \left[\frac{\partial^2 E}{\partial v^2} \right]_{v_0}$$

where v_0 is the equilibrium volume per unit cell, which is connected to the equilibrium lattice constant a_0 by $v_0 = \frac{1}{2} a_0^3$. The trends of changes of the bulk modulus B are the same as those of the cohesive energy. In the basis set of $8s1p$, the value of B obtained from Li_{15} is 8.9×10^{10} dyn/cm^2 which is in good agreement with the experimental value of 11.5×10^{10} dyn/cm^2 (Ref. 5 and references therein). Rao *et al.*[5] obtained a value of 12.6×10^{10} dyn/cm^2 for B using a 15-atom cluster similar to ours. We should note that the band calculation for B is 13.8×10^{10} dyn/cm^2 (Ref. 15) and the free-electron value for B is 23.9×10 dyn/cm^2.[5]

The integrated density of states of Li_{15} calculated at the bulk lattice constant of lithium in the basis set of $8s1p$ is in very good agreement with that of a band calculation, while that of Li_9 is totally in disagreement. The energy gap is about 43 eV, which is not sensitive to the size of the cluster and of the basis set.

In our calculations, we find that the difference of the $1s$ orbital energies between different atoms in Li_9 is greater than 0.1 Ry in all basis sets except the $4s$ one, while in Li_{15} this value is about an order smaller. The smallest difference is obtained from Li_{15} in the basis set of $8s1p$. This perhaps can give us some information about how well a cluster model can describe the bulk since in solids the $1s$ energy levels of atoms become a very narrow energy band.

We would like to point out that one must be careful in the choice of the initial input charge density in the self-consistent calculations using local-density-functional theory. In our calculations, the total energies of Li_9 and Li_{15} in a spin-polarized calculation, in which the input configuration of the Li atom is $(1s)^2(2s)^1$, is about 0.004 Ry lower than that in a non-spin-polarized calculation. There is also an unpaired electron in the cluster. If one used the spin-polarized calculation, one would obtain spurious magnetic moment. This conclusion agrees with that of Redfern *et al.*[6] In the case of Li_6Mg which we shall describe below, the final results are independent of the initial description of the atoms just like that in the study of SF_6 by Tang and Callaway.[10]

B. Li_6Mg

Recently, Rao and Jena[8] made an elaborate study of the electronic structure and geometry of heteroatomic clusters using the unrestricted Hartree-Fock (UHF) method augmented by configuration interaction. After

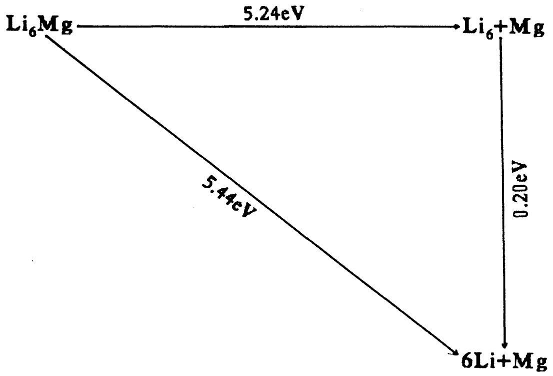

FIG. 1. Atomization energy of Li_6Mg obtained by different procedures.

optimization for the geometry of the clusters, they found that the importance of Jahn-Teller distortion in a strongly bonded compound is significantly reduced. The geometry of Li_6Mg is simply a simple cubic. Lee, Callaway, and co-workers[1,2,4] successfully studied the electronic properties of the impurities in solid from the model of the cluster in the framework of local spin density functional theory (LSDA). As is well known, a point defect in a solid perturbs the host electron distribution and the arrangement of the host atoms in the vicinity of the defect. But these perturbations are usually small and are confined to a local environment. In the rest of this paper, we will present our results for Li_6Mg in the framework of LSDA.

Besides the fact that the method employed in our calculations for Li_6Mg is different from that of Rao and Jena, the basis sets are also different. The equilibrium lattice constant of Li_6Mg in the present work is 2.477 Å, which is in excellent agreement with that of 2.48 Å obtained by Rao and Jena. As usual, the total energy of −486.649 41 Ry from LSDA calculation is higher than that of −487.059 38 Ry obtained from UHF calculation.

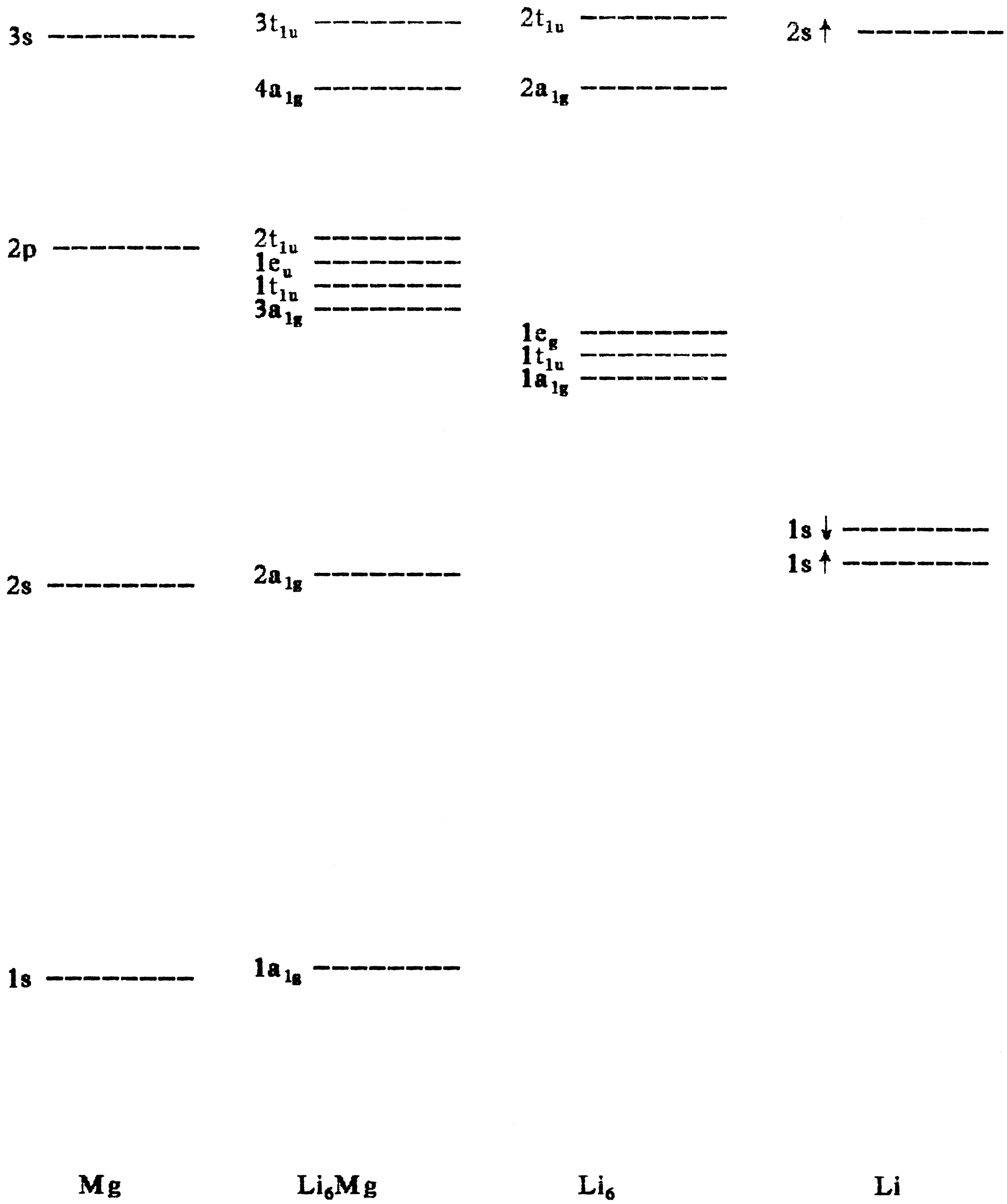

FIG. 2. Schematic occupied energy level diagram for atoms of Li and Mg and for clusters of Li_6 and Li_6Mg. The difference between levels in energy is not the real scale of the corresponding atoms and the corresponding clusters.

The atomization energy which is defined by Rao and Jena as the (positive) energy needed to split the cluster to its constituent atoms in the present calculation is 5.44 eV. This value is smaller than that of 11.707 eV obtained by Rao and Jena. To test our result, we recalculated the total energy of Li_6 which was obtained by removing the Mg atom from the cluster of Li_6Mg at the equilibrium lattice constant of Li_6Mg. The result is $-88.674\,626$ Ry. Thus the energy needed to split the cluster to a Mg atom and Li_6 is only 0.20 eV and the energy needed to split the cluster of Li_6 to six isolated Li atoms is 5.24 eV. This procedure is diagrammatically shown in Fig. 1. Here we see that the same result for the atomization energy is obtained. Hence we believe our calculations are reliable in the framework of LSDA. We do not know exactly the reason for the discrepancy in these two calculations. But the basis set may have some effects. Rao and Jena did not use the *d*-like functions in their calculations. They did not have the *d*-like charge on the Mg atom, while there is 0.012 of an electron residing at the Mg atom in our calculation. Collins *et al.*[14] proved that the *d*-like functions are very important for correctly describing the properties consisting of the elements in the third period in the Periodic Table.

We are now to see the processes in the formation of Li_6Mg from the isolated atoms. We plot in Fig. 2 schematically the energy levels of atoms of Li and Mg and of clusters of Li_6 and Li_6Mg at the equilibrium lattice constant. From this figure, we see that in forming Li_6, the two separated 1*s* levels of free Li atoms become one level in Li_6 which two paired electrons occupy. The highest level $2t_{1u}$ only has one electron on it. After the Mg atom which contains 12 electrons is placed at the center of the cluster, the highest level is fully occupied by electrons. Therefore the Li_6Mg should be a relative stable cluster considering that there is no partially occupied state which causes the so-called pseudo-Jahn-Teller effect. From the Mulliken population analysis of Li_6Mg, we know that the Mg atom gives out 1.13 electrons, which are shared by the six Li atoms surrounding it. This result agrees well with that of Rao and Jena.[8] Here, the behavior of the central atom is totally different from that in Li_7.[17] In Li_7, the central atom has extra electrons on it and most of the unpaired electron is residing on it, while in Li_6Mg, the central atom gives out its charge to its neighbors and has no net charge on it since there is no unpaired electron in this cluster.

The ionization potentials of Li_9, Li_{15}, and Li_6Mg, which is 5.32 eV calculated in the present work, are systematically larger than those found by the other calculations. This may relate to the difficulty of LSDA in predicting accurate values for the ionization potentials.[10]

IV. CONCLUSIONS

We have performed self-consistent calculations for Li_9, Li_{15}, and Li_6Mg in the framework of local-density-functional theory. The main conclusions are that the basis set is of essential importance to clusters when clusters are used as a model to describe the properties of bulk. Fortunately, a well-chosen basis set exists in which the cluster has many properties of the bulk. This leads us to consider the cluster as a portion of a solid and in a special subspace of basis functions the cluster can represent the solid. Of course, in doing so, the size of the cluster should be large enough. But the question of what the criteria are and how we search the subspace of basis functions is still open. In forming Li_6Mg, the central atom gives out its charge to its neighbors to form a stable cluster.

ACKNOWLEDGMENTS

This work was supported by the Chinese National Science Foundation. The author thanks Professor Yichun Zhao and Professor Zhije Zhang for their help in the calculations. The author is indebted to Professor Joseph Callaway for his kind assistance during the author's stay in the U.S.A.

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