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Effect of Symmetry Breaking on Hydrogen Site Preference in Small Metal Clusters

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The total energies of hydrogen interacting with small clusters of lithium atoms have been calculated self-consistently by means of the unrestricted Hartree-Fock scheme. The total energy is found to be lowered when hydrogen moves away from the most symmetric site in the cluster. This observation is independent of the cluster geometry as long as its size remains small. These results, which are analogous to Jahn-Teller distortion, have important consequences on cluster calculations designed to mimic the bulk solid.

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One of the most popular theoretical methods for calculating the electronic structure of defects in metals in recent years has been based on the molecular-cluster approach.[1-3] Here, a defect in an infinite crystal is modeled by a cluster of a few host atoms surrounding the defect. It is then hoped that this limited number of atoms in the cluster can simulate the properties associated with the interaction of the defect with host atoms in an infinite system.

The equilibrium site of the impurity can be studied by finding the minimum in the total energy of the cluster for various assumed impurity configurations. In this Letter we point out that the energetics of an interstitial impurity depends strongly on the cluster size as well as the geometry of the cluster atoms surrounding it. This observation is the result of calculations of the total energies of a hydrogen atom interacting with small clusters of lithium atoms using unrestricted Hartree-Fock theory in the molecular-orbital representation. A universal feature of our calculations is that the energy of hydrogen is lowered when it moves away from its most symmetric position in the cluster to a nearest interstitial site, irrespective of how the cluster is constructed as long as its size remains small. The source of this energy lowering is shown to lie in the nature of the screening of the hydrogen charge and its bonding-antibonding characteristics. This energy lowering by symmetry breaking is analogous to Jahn-Teller distortion.[4] We discuss our results *vis á vis* other theoretical methods. We also point out inherent difficulties associated with the cluster approach for studying defect energetics in bulk solids.

We write the molecular orbital ψ_i of the defect cluster as a linear combination of atomic orbitals ϕ_μ, namely,

$$\psi_i(\vec{r}) = \sum_\mu C_{\mu i}\phi_\mu(\vec{r}). \tag{1}$$

Here the index μ runs over all the atoms and all the oribtals of atoms in the cluster. A hydrogen atom is located at an interstitial position in the cluster. The coefficients $C_{\mu i}$ are varied until the energy of the cluster becomes self-consistent. The atomic orbitals ϕ_μ were constructed from Gaussian-type orbitals. For lithium atoms we have used the well-known STO-3G basis set.[5] For the hydrogen atom the conventional basis set for $1s$ orbitals was augmented with optimized $2s$ and $2p$ orbitals to take into account effects associated with polarization.

We have investigated clusters symmetric around both tetrahedral and octahedral sites and containing up to three nearest-neighbor (NN) shells of Li atoms. For the tetrahedrally symmetric cluster we have four NN, four second-NN, and eight third-NN host atoms while for the octahedrally symmetric cluster we have two NN, four second-NN, and eight third-NN host atoms.

For clusters containing four tetrahedrally symmetric lithium atoms (up to first NN around hydrogen) and six octahedrally symmetric lithium atoms (up to second NN around hydrogen) the total energies were calculated for a continuous (in steps of $0.1a_0$) variation of the position of hydrogen between O and T sites. In Fig. 1 we plot the total energies measured with respect to the O site. For the cluster most symmetric about the T site, the energy of hydrogen decreases as it moves towards the O site. The results for the cluster symmetric about the octahedral site are just the opposite. Here, the

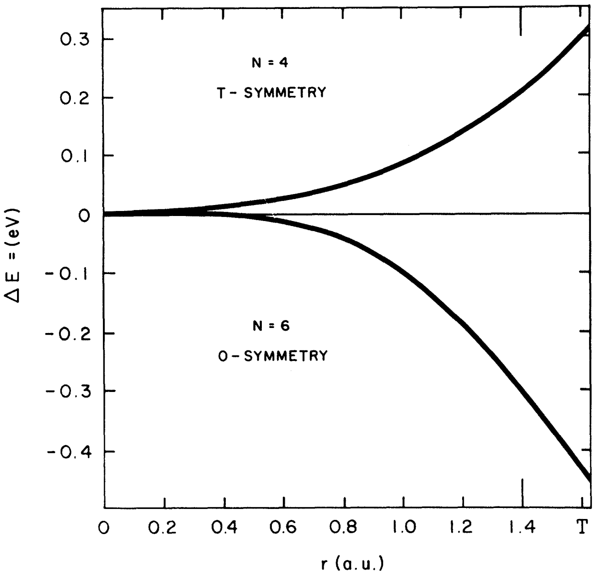

FIG. 1. The spatial dependence of the energy of hydrogen measured with respect to the energy at the octahedral position. The curves for the tetrahedrally symmetric four-atom cluster and the octahedrally symmetric six-atom cluster are shown separately.

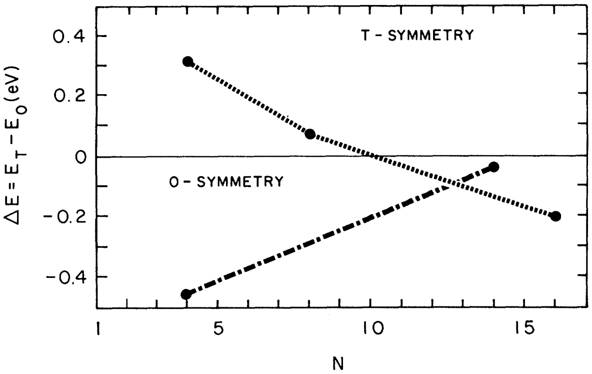

FIG. 2. The energy difference between tetrahedral and octahedral sites of hydrogen ($\Delta E = E_T - E_O$) for clusters symmetric about tetrahedral sites ($N = 4, 8, 16$) and octahedral sites ($N = 6, 14$).

energy of hydrogen at the T site is lower than that at the O site. In order to examine whether the tendency of hydrogen to move from the most symmetric site to a site of lower symmetry is dependent on the cluster size, we have calculated total energies for larger clusters containing eight, fourteen, and sixteen lithium atoms. Since these calculations are costly and time consuming, we have computed the total energies at two locations only, i.e., by placing hydrogen at T and O sites in each of these three clusters. The energy difference $\Delta E = E_T - E_O$ for these clusters along with those in four- and six-atom clusters are plotted in Fig. 2. For the sake of clarity, we have presented results for clusters with O and T symmetry separately. It is clear that hydrogen prefers to occupy a less symmetric site in the clusters containing less than sixteen lithium atoms. This tendency is independent of the geometry of the clusters. We shall comment on the magnitude of the energy differences ΔE in Fig. 2 versus cluster size and their relationship to bulk behavior later in this Letter.

The lowering of the energy in going to a less symmetric hydrogen site in small clusters can be understood as an effect of symmetry breaking. For the simplicity of argument, we first consider clusters with spherical symmetry (e.g., jellium clusters) where the electron levels can be classified in terms of the angular momentum quantum number. At the center of the cluster only s levels contribute to the electron density, and most of it comes from the lowest s state. When the hydrogen is at the center of the cluster, only s states contribute to the screening at small distances. Because of the small number of these levels the screening is less effective in a small cluster than in an infinite solid. Once hydrogen is displaced from the center of the cluster, all electron states (i.e., electrons with all angular momentum values) contribute to the screening. Thus, the screening of hydrogen at short distances can be more complete when hydrogen is at an off-center position than when it is at the center of symmetry. It is then expected that the energy is lowered when the hydrogen is moved from the high-symmetry site to a site where the electron screening has a more collective character.

In clusters consisting of real atoms the symmetry at the center is never as high as in the spherical case. However, for real clusters the site with highest symmetry still has the smallest number of states contributing to the local electron density. This is demonstrated in Fig. 3 which shows the local density of states $|\psi_i(\epsilon_i,r)|^2$ at the octahedral and tetrahedral sites in the fourteen-atom cluster. At the O site only four electrons (two spin-up and two spin-down) have nonzero density, whereas at the T site ten electrons contribute to the density. In small clusters it is then expected that a lowering of the symmetry of the hydrogen site will lower the total energy in a way similar to that by which the removing of degeneracy by lattice distortion lowers the energy in the Jahn-Teller effect. The symmetry breaking becomes especially important for hydrogen in metallic clusters because the hydrogen forms a doubly occupied bound state just below the lowest valence electron level of the metal. The contribution of this valence electron level is overem-

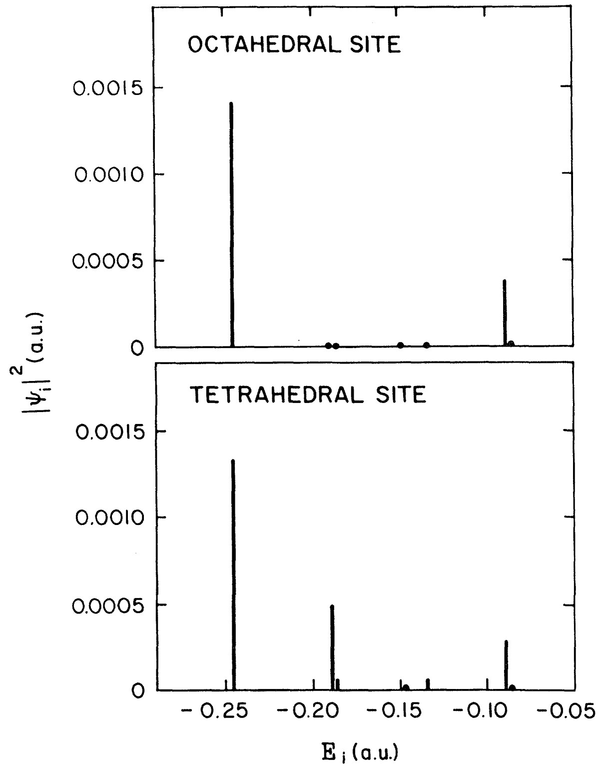

FIG. 3. The ambient valence electron density of states $|\psi_i|^2$ for the fourteen-Li-atom cluster (without any hydrogen) at the octahedral and tetrahedral sites.

phasized in the center of symmetry and its coupling to the close-lying hydrogen bound state overemphasizes the antibonding.

It is now appropriate to relate these results to calculations in infinite systems. The primary purpose of such a discussion is to determine the size of clusters needed to mimic the energetics of hydrogen in bulk metals. For a crystalline material consisting of an infinite number of atoms, it is immaterial whether the crystal is constructed about the *T* or the *O* site. The equilibrium position of hydrogen in an infinite solid is always uniquely given. For the tetrahedrally symmetric cluster containing sixteen lithium atoms we find that hydrogen prefers the *T* site. This is in contrast to results obtained from four- and eight-atom clusters. For the octahedrally symmetric fourteen-atom cluster hydrogen also prefers the *T* site. Thus, one may be tempted to conclude that the energetics of hydrogen exhibit bulklike behavior in clusters containing as few as fourteen atoms. We believe that such an optimism is premature since the magnitude of the energy differences ΔE between the *O* and *T* sites in fourteen- and sixteen-atom clusters differ by an order of magnitude from each other although they (ΔE) are of the same sign. To illustrate this point further we considered a $Li_{14}H$ cluster which was constructed differently from the original $Li_{14}H$ geometry. Here the two octahedral sites were inequivalent in the sense that they had identical near neighbors up to third-NN sites, but different farther neighbors. The total self-consistent energies of hydrogen at these two octahedral sites differed by 1.6 eV. Similar dependences have been observed by Shillady and Jena[6]. Thus, caution has to be exercised while relating the energetics of impurities in small clusters to the bulk state.

The calculations[7] for hydrogen in alkali metals reveal that the preferential interstitial site is the tetrahedral site. There the leading term in determining the site dependence of the energy is the electrostatic Madelung energy resulting from the interaction of the proton with a lattice consisting of point ions and a homogeneous electron gas. The structural dependence in this term comes solely from the Coulomb repulsion of the positive ions:

$$E_C = \sum_i (1/|\vec{r}_H - \vec{r}_i|), \tag{2}$$

where $\vec{r}_H$ and $\vec{r}_i$ are respectively the position vectors of hydrogen and nuclei. If this is calculated for clusters containing up to fourteen lithium atoms, the result is that the hydrogen is always pushed out from the center of symmetry in agreement with the self-consistent results. In small clusters, however, one cannot neglect the electrostatic term arising from electrons even if they are assumed to form a homogeneous gas. Unfortunately, a spherical approximation for the electron distribution is not very meaningful since the surface of the cluster would not be properly described. Although in small clusters the electrostatic repulsion from lithium ions seems to give qualitatively the same result as the self-consistent calculation, one cannot, as in the infinite solid, predict the preferential hydrogen site on the basis of electrostatic considerations alone. For example, in the sixteen-atom cluster considered here the electronic energy dominates over the nuclear repulsion term.

Model calculations for hydrogen in spherical jellium clusters have shown[8] that the binding energy of hydrogen in the cluster depends very much on the size of the cluster. The filling of new energy states with increasing cluster size creates structure on the energy versus cluster size curve. This requires cluster sizes of about 100 atoms before the binding energy in the bulk can be estimated within an accuracy of 0.2 eV. In metal clusters containing real atoms the degeneracy is smaller than that in jellium. Thus the asymptotic value of the energy difference is expected to be reached faster.

Recently in studies[9] involving the chemisorption of hydrogen and other atoms on metal surfaces, various authors have noted that the chemisorption energies and bond lengths of chemisorbed atoms depend on the atomic structure of metal surfaces. Our observation, however, is not related to the above results for the following reasons. Once a particular metallic surface is chosen for chemisorption studies, the atomic positions on this surface are uniquely specified. The situation in the studying of energetics of interstitial impurities in the bulk is, on the other hand, entirely different. As shown in this Letter, one has a lot of freedom in choosing the cluster geometry. The important result of this Letter is that the energetics of interstitial impurities are dependent on how the cluster is constructed and caution, therefore, must be exercised in predicting the equilibrium impurity site from calculations based upon the cluster approach.

In conclusion, we have carried out self-consistent, unrestricted Hartree-Fock calculations of total energies of several lithium-atom clusters interacting with hydrogen. The main results are as follows: (1) In small metal clusters hydrogen moves from the most symmetric site to the nearest interstitial site. This observation is analogous to the Jahn-Teller effect. (2) The screening requirement of hydrogen charge dictates its preferential site in a small cluster. (3) The energy difference between two different interstitial sites depends on the cluster chosen. Even though the site preference of hydrogen can be qualitatively predicted from cluster calculations of about sixteen host atoms, the quantitative prediction of activation energy for diffusion cannot be made on the basis of calculations on small clusters. This makes it necessary to view with caution the cluster calculations designed to mimic the impurity energetics in an infinite solid.

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