# Density Functional Study of $Li_nH_m$ Clusters. Electric Dipole Polarizabilities

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*Received: July 21, 1998; In Final Form: November 6, 1998*

The dipole polarizability of a series of clusters of the type $Li_nH_m$ has been calculated using density functional methods. The study of the trends in the mean polarizability and the anisotropy are explained in terms of the interplay between electronic and geometrical effects. The changes in the polarizability for different isomers of a given cluster as well as its variations when hydrogen atoms are added to a given cluster are also discussed. A very related quantity, the hardness, has also been calculated in the simple approximation of hardness equal to the energy gap. Their values are discussed in terms of the possible stability of the different clusters.

## Introduction

The theoretical and experimental study of the polarizabilities of metal clusters is an area of growing interest. They are important for understanding the size dependence of optical properties of small particles. The chemical bonding is profoundly changed in the formation of a cluster whereas the solid-state-like properties like the dielectric constant are of no significance in a cluster of few atoms. The dipole polarizability, however, represents a suitable molecular property that can take on the role of the dielectric constant and can be measured without touching the cluster.[1] The dipole polarizability comprises the information of the bonding character in the cluster, and on the other hand, through the Classius−Mosotti relation it yields information about the dielectric constant of the solid-like macroscopic particle formed with the cluster. The experimental measurement of cluster polarizabilities is relatively easy in comparison to other properties of neutral clusters. In the presence of an electric field the neutral clusters are deflected in linear order due to their dipole polarizabilities,[1−3] allowing their measurement. Hence, the polarizabilities can be one of the most important pieces of information about the nature of the bonding and the geometrical structure of the neutral clusters. To fulfill this goal, it is necessary to have a reliable theoretical model to understand the principal factors influencing the polarizabilities. The jellium model has been successfully applied to study the polarizability of large clusters approaching the bulk properties.[4] For small clusters, however, one expects more bonding and geometrical effects than those incorporated in the jellium model. Therefore, ab initio calculations are necessary, and the experience gained in calculating the dipole polarizabilities of atoms and molecules is useful. Since the theoretical calculation of the dipole polarizability is a very demanding computational job, there are few ab initio calculations of the dipole polarizability of clusters.[5−9] However, the importance of polarizabilitiy data to rationalize experimental observations has been recently stressed,[1] justifying the effort of looking for reliable theoretical models to calculate it and make valuable suggestions for further experiments.[10]

In this paper the hydrogenated lithium clusters of the type $Li_nH_m$ ($n, m \leq 4$) have been studied. These clusters have been of large interest as prototypes for the study of a possible metal−insulator transition and also as a model for a metallic cluster on the surface of an ionic insulator.[11] These clusters are also very good models for the study of the competition between the ionic and covalent parts in hydrogen bonding.[12] Kato et al.[13] studied the hydrogenated lithium clusters at the SCF level with a small basis set. Nevertheless, their geometrical predictions are qualitatively correct with few exceptions. The small members of the series of clusters were also studied at the SCF level by Cardelino et al.[14] After that, Rao et al.[15] calculated the equilibrium geometry, binding energy, and stability of some $Li_nH_m$ clusters by taking into account the correlation effects by means of MP2. The most recent work is the one of Bonacic−Koutecky et al.[16] They did an exhaustive geometry optimization at the CI level of calculation, checking for different isomers. They calculated ionization potentials, binding energies, and excitation energies. The structure of the $Li_nH_m$ clusters is very simple. In fact, they are the simplest mixed systems that can be built. However, they present the interesting phenomenon of separation of a metallic part and an insulating part. Recent experiments[12] have shown, for instance, that for the quasi-stoichiometric clusters $(LiH)_nLi^+$ a total loss of the metallic character is observed. New experiments have been also done to investigate the evolution from the sparsely hydrogenated clusters, which display metallic features, to the hydrogen saturated clusters, which display nonmetal features.[17] This transition should have an important effect on the polarizability of the clusters. Coming back to the paper of Rao et al.,[15] they found that the hydrogen uptake by a cluster does not exceed that in the bulk. However, the ionization potentials are strongly affected by the hydrogen content of the cluster. The ionization potentials steadily increase with increasing hydrogenation and undergo a sudden change when the cluster reaches its hydrogen saturation. In terms of HOMO levels, the explanation is clear.[15] As hydrogen is added, the ionization potential increases because of the charge transfer from the Li 2s to H 1s state with the consequent lowering of the HOMO level. The sudden change occurs when the hydrogen-induced levels are enough to be occupied for all the valence electrons of the cluster. In this case the HOMO level changes from being a delocalized state over all the lithium atoms to being a hydrogen-localized state. This is the origin of the abrupt change in the ionization potentials when the number of hydrogen atoms is the same as the number of lithium atoms. This fact, which is clearly related to the metal−

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10.1021/jp983105l CCC: $18.00

insulator transition, has been one of the principal motivations to study the variation of the dipole polarizability as hydrogen is added to the lithium clusters. In general, because the polarizability should be proportional to the volume of the cluster, it is expected that it increases when more atoms are added to the system. However, for the $Li_nH_m$ clusters the energy gap augments when hydrogen atoms are added to the cluster, and from simple perturbation theory, one should expect a lowering of the polarizability. In this paper, we will show that the second argument prevails. From another point of view, already the comparison of the atomic polarizabilities is illuminating. The lithium atom has a very diffuse valence density and, consequently, a large polarizability $\alpha = 164$ au.[18] Hydrogen atom has a compact density and a small polarizability $\alpha = 4.5$ au. Since the LiH bonding is polar with an important charge transfer to the hydrogen atom, one can expect a polarizability more similar to a negative hydrogen atom.

The theoretical study of electronic properties of clusters formed by a small amount of atoms has been markedly dominated by the density functional based methods, specially the Kohn−Sham method. However, contrary to the situation in the metals where the local approximation (LDA) performs well, for clusters it is necessary to incorporate corrections to the local models. The gradient-corrected versions of the LDA have been widely applied to clusters, confirming the reliability of the results for energetic properties of the ground state. For the calculation of the dipole polarizability the use of density functional based methods could be more questionable. It is known that the actual exchange-correlation functionals are not able to yield accurate results for van der Waals interactions.[19] Therefore, the same should occur in regard to polarizability calculations. In fact, it has been demonstrated that the exchange-correlation potentials derived from the commonly used functionals do not have the correct asymptotic behavior.[20] This has a strong influence in the calculated polarizabilities. However, while this is certainly the case for atoms, it seems that for a conglomerate of atoms the bonding structures are more important than the asymptotic behavior of the potential.[21] Hence, we are in a situation where a property, the dipole polarizability, is calculated with more accuracy for the more complicated systems (molecules and clusters) than it is for the simpler systems (atoms). DFT methods have been used for the calculation of dipole polarizabilities of clusters of sodium by Moullet et al.[22] and more recently by Guan et al.,[23] and they will be also used in this work.

Density functional theory has also been very useful in providing a formal framework to many chemical reactivity indices, such as electronegativity,[24] hardness,[25] and the Fukui function.[26] In particular, the global hardness yields information about the stability of the electronic system. A principle of maximum hardness has been postulated.[25] It says that a species is more stable the greater is its hardness. Very recently, Chattaraj and Sengupta,[27] using a known inverse relationship between hardness and polarizability,[28] have postulated a minimum polarizability principle. It says, the natural direction of evolution of any system is toward a state of minimum polarizability. It is, therefore, highly interesting to calculate the hardness of the studied clusters.

## Methods

**Density Functional Methods.** Our calculations were carried out at the all-electron level using the GAUSSIAN94 package,[29] where a variety of density functional schemes are implemented. Besides the simplest local density functional approximation (LDA), several functionals including gradient corrections are included. In atoms and molecules it has been already shown that the hybrid functionals performs better in calculations of polarizabilities.[21] They are characterized by the inclusion of a part of the Hartree−Fock exchange calculated with the Kohn−Sham orbitals. This corrects in part for the wrong asymptotic behavior of the exchange-correlation potential. Hence, the functional B3PW91 proposed by Becke[30] has been used. The now most popular B3LYP version of the Gaussian company[29] has been also tested for some systems, and the results are very similar.

It is well-known that the calculation of the dipole polarizability is very sensitive to the quality of the basis set. It is necessary to include extra diffuse functions to describe the distortions of the electron density due to the external electric field. On the other hand, sometimes the errors inherent to the theoretical method are in the opposite direction with respect to the errors produced by the basis set. Hence, a careful calibration of the basis set can achieve a compensation of errors, producing a final result better than expected, which, however, cannot be extrapolated to other types of systems. In this paper, two basis set have been used: the well-known 6-311G** basis set incorporated into the GAUSSIAN94 package and the medium size polarized basis set derived by Sadlej,[31,32] which is of the type 10s6p4d/[5s3p2d] for Li and 6s4p/[3s2p] for the H. The 6-311G** basis set has been constructed to give a good representation of the bonding and geometrical structure of molecules. The Sadlej basis set has been constructed specially for the calculation of electric properties such as the dipole moment and dipole polarizabilities.

**Polarizability Calculations.** The definition of the electric dipole polarizability can be taken from the Taylor expansion of the total energy in the components of the uniform electric field $\vec{F}$ [33]

$$E = E_0 - \mu_\alpha F_\alpha - \frac{1}{2}\alpha_{\alpha\beta}F_{\alpha\beta} - ... \tag{1}$$

where $E_0$ is the energy in the absence of the electric field,

$$\mu_\alpha = -\left(\frac{\partial E}{\partial F_\alpha}\right)_{\vec{F}=0} \tag{2}$$

is the dipole moment, and

$$\alpha_{\alpha\beta} = -\left(\frac{\partial^2 E}{\partial F_\alpha F_\beta}\right)_{\vec{F}=0} \tag{3}$$

is the dipole polarizability tensor. The subindices $\alpha$ and $\beta$ stand for the Cartesian coordinates $x$, $y$, and $z$. In eq 1 the Einstein sum convention has been used. The experimentally acceptable quantities are the mean polarizability

$$\langle\alpha\rangle = \frac{1}{3}\mathbf{tr}(\alpha) \tag{4}$$

and the polarizability anisotropy

$$\gamma^2 = \frac{1}{2}[3\mathbf{tr}(\alpha^2 - (\mathbf{tr}\alpha)^2)] \tag{5}$$

The second derivative of the energy with respect to the electric field can be done analytically for almost any density functional scheme. However, for the purpose of checking the accuracy of the results, sometimes $\alpha$ can be calculated as the first derivative of the induced dipole moment with respect to the electric field. This derivative can be done numerically. In this paper, both types of calculations have been done.

**Hardness.** In density functional theory the hardness, $\eta$, has been defined as the second derivative of the energy with respect to the number of electrons:[25]

$$\eta = \left(\frac{\partial^2 E}{\partial N^2}\right)_v \tag{6}$$

Note that in the original definition was a factor one-half in the right-hand side of eq 6, which has been dropped.[34] A more operational definition can be obtained by making use of the finite difference approximation:[25]

$$\eta = I - A \tag{7}$$

where $I$ and $A$ are the ionization potential and the electron affinity of the system, respectively. Assuming the validity of the Koopmans' theorem, eq 7 can be written as

$$\eta = \epsilon_{\mathrm{LUMO}} - \epsilon_{\mathrm{HOMO}} \tag{8}$$

where $\epsilon_{\mathrm{LUMO}}$ and $\epsilon_{\mathrm{HOMO}}$ are the lowest unoccupied and the highest occupied molecular orbital energies, respectively. It coincides exactly with the energy gap of a solid, and there is a lot of evidence that a large gap increases stability. For an open-shell system the given approximation for the hardness is not complete because it is necessary to consider the spin. Two possibilities have been discussed in the literature,[35-38] the first one takes the average between the gap for spin up and down, respectively, and the second one, which has been used in this work, takes the minimum between the gaps for spin up and down. Both models yield very similar results. The reason lies in the physical argument of avoiding to add into the hardness the energy of the spin-flipping. A recent overview of the hardness concept and energy gap can be found in ref 39. In this work the hardness has been calculated using eq 8.

## Results and Discussion

The geometries of all the clusters studied in this work are displayed in Figure 1. No attempt has been done to calculate the most stable geometrical structure of each cluster. There are several works devoted to it, and the density functional methods have already proved to yield reasonable results.[40] Hence, the geometries have been taken from the work of Rao et al.,[15] or from the new one of Bonacic-Koutecky et al.[16] In some cases, two different isomers have been calculated in order to understand the dipole polarizability variations. In particular, for $Li_4H_3$ and $Li_4H_4$, the most stable structures are the ones derived from a tetrahedral $Li_4$ structure. However, starting from the $Li_4$ cluster and adding the hydrogen atoms one to one, the planar structures are expected. Hence, we have calculated both of them. For the isomers that are not included in the referenced works, the angles and bond lengths were not relaxed. Numerical experimentation varying the geometrical parameters shows small variations in the dipole polarizability that cannot affect our qualitative discussion of the results.

In Table 1, results for atomic lithium and the diatomic molecules $Li_2$ and LiH are shown. They have been obtained using the 6-311G** basis set and are useful for calibrating the reliability of the cluster calculations. One can see that for $Li_2$ the dissociation energy is lower than the experimental one and that the opposite is true for LiH. The calculated dipole polarizabilities, mean values, and anisotropies compare very well with the CI results obtained by Sadlej et al.[32,41] Hence, one can have some confidence in the results obtained for the clusters using the same basis set. Nevertheless, some check calculations using the Sadlej basis set have been done, and they will be discussed later on.

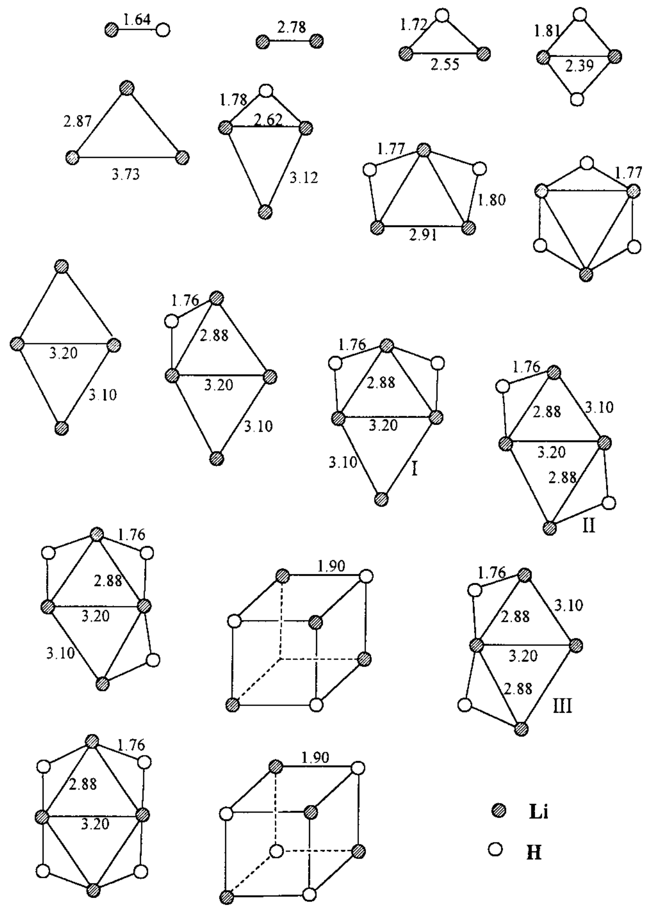

**Figure 1.** Geometries of the studied clusters. The bond lengths are given in au. The ground state of the clusters with an even number of electrons is a singlet and a doublet for the clusters with an odd number of atoms.

**TABLE 1: Results for Li, $Li_2$, and LiH**

| | $E$ (au) | $D_e$ (eV) | $\gamma$ (au) | $\langle\alpha\rangle$ (au) |
|---|---|---|---|---|
| Li($^2S$) | −7.483 812 | | | 150 (172)[b] |
| $Li_2$($^1\Sigma$) | −14.997 178 | 0.804 (1.06)[a] | 109 (141)[c] | 211 (216)[c] |
| LiH($^1\Sigma$) | −8.074 328 | 3.034 (2.52)[a] | 2.17 (3.3)[b] | 27.8 (28.9)[b] |

[a] Reference 42. [b] Reference 32. [c] Reference 41.

In Table 2, for each cluster studied in this work the total energy, the atomic binding energy per atom $\Delta E_a$, the hydrogen binding energy per atom, $\Delta E_b$, and the energy of the highest occupied molecular orbital (HOMO) have been displayed. The atomic binding energy increases steadily when the number of atoms augments and shows the characteristic even−odd alternation, especially in comparing clusters with the same number of hydrogen atoms. The hydrogen bonding energy has very small variations. It lies between 3.8 and 3.9 eV for almost all the clusters showing also a small even−odd alternation effect. The almost constancy in the hydrogen bonding energy means that the saturated clusters, $Li_nH_n$, will be preferred. That makes more difficult the observation of the other clusters. The $Li_nH_n$ clusters show a dramatic effect in the HOMO energy. The HOMO energy has small variations when the first hydrogen atoms are added to the cluster but increases sharply at the saturation level. Through the Koopmans' theorem, the HOMO energy can be associated with the vertical ionization potential. The great

**TABLE 2: Ground State Energies $E$, Atomization Energy $\Delta E_a$, Hydrogen Binding Energy $\Delta E_b$, and HOMO Energy $\epsilon_H$ of Neutral $Li_nH_m$ Clusters**

| | $E$ (au) | $\Delta E_a/(m+n)^a$ (eV) | $\Delta E_b/n^b$ (eV) | $-\epsilon_H$ (eV) |
|---|---|---|---|---|
| $Li_2(^1\Sigma)$ | −14.997 178 | 0.40 | | 3.65 |
| $Li_2H(^2A_1)$ | −15.598 532 | 1.38 | 3.33 | 3.11 |
| $Li_2H_2(^1A_g)$ | −16.224 528 | 2.03 | 3.66 | 5.49 |
| $Li_3(^2B_2)$ | −22.502 082 | 0.46 | | 3.07 |
| $Li_3H(^1A_1)$ | −23.125 577 | 1.33 | 3.93 | 3.54 |
| $Li_3H_2(^2A_1)$ | −23.739 075 | 1.79 | 3.80 | 3.52 |
| $Li_3H_3(^1A_1)$ | −24.367 282 | 2.17 | 3.88 | 5.89 |
| $Li_4(^1A_9)$ | −30.023 851 | 0.60 | | 3.21 |
| $Li_4H(^2A_1)$ | −30.638 408 | 1.22 | 3.69 | 3.31 |
| $Li_4H_2(I)(^1A_1)$ | −31.266 659 | 1.69 | 3.88 | 3.81 |
| $Li_4H_2(II)(^1A_g)$ | −31.233 429 | 1.54 | 3.42 | 3.20 |
| $Li_4H_2(III)(^1A_1)$ | −31.247 462 | 1.61 | 3.61 | 3.64 |
| $Li_4H_3(I)(^2A_1)$ | −31.873 619 | 1.95 | 3.74 | 3.89 |
| $Li_4H_3(T_h)(^2A_1)$ | −31.888 883 | 2.01 | 3.88 | 3.21 |
| $Li_4H_4(I)(^1A_g)$ | −32.503 803 | 2.22 | 3.84 | 6.60 |
| $Li_4H_4(T_h)(^1A_1)$ | −32.520 914 | 2.28 | 3.95 | 5.83 |

[a] $\Delta E_a/(m+n) = -[E(M_nH_n) - nE(M) - nE(H)]/(m+n)$. [b] $\Delta E_b/n = -[E(M_nH_n) - E(M_n) - nE(H)]/n$.

**TABLE 3: Some Properties of Neutral $Li_nH_m$ Clusters: Anisotropy $\gamma$, Mean Polarizability $\langle\alpha\rangle$, and Hardness $\eta$**

| | $\gamma$ (au) | $\langle\alpha\rangle$ (au) | $\eta$ (eV) |
|---|---|---|---|
| $Li_2$ | 109 (115)[a] | 211 (217)[a] | 2.22 |
| $Li_2H$ | 270 | 192 | 1.71 |
| $Li_2H_2$ | 12.3 (13.3)[a] | 34.5 (34.6)[a] | 5.05 |
| $Li_3$ | 298 | 341 | 1.49 |
| $Li_3H$ | 47.1 | 196 | 2.21 |
| $Li_3H_2$ | 32.7 (20.6)[a] | 126 (134)[a] | 2.64 (2.58)[a] |
| $Li_3H_3$ | 12.3 (6.14)[a] | 52.4 (57.1)[a] | 5.72 (5.63)[a] |
| $Li_4$ | 333 | 379 | 1.60 |
| $Li_4H$ | 215 | 316 | 1.98 |
| $Li_4H_2(I)$ | 48.3 (47.9)[a] | 194 (199)[a] | 2.52 (2.50)[a] |
| $Li_4H_2(II)$ | 290 (285)[a] | 244 (255)[a] | 1.22 (1.21)[a] |
| $Li_4H_2(III)$ | 123 (116)[a] | 227 (230)[a] | 1.81 (1.81)[a] |
| $Li_4H_3(I)$ | 35.7 | 129 | 2.84 |
| $Li_4H_3(T_h)$ | 19.8 | 159 | 2.57 |
| $Li_4H_4(I)$ | 17.0 | 69.3 | 5.87 |
| $Li_4H_4(T_h)$ | 0 | 73.0 | 5.49 |

[a] Basis set, ref 31.

stability of the $Li_nH_n$ clusters against ionization was already explained by Rao et al.[15] and described in the Introduction.

Some other binding energies are also interesting. For instance, the energy to dissociate in LiH molecules: $Li_nH_n \rightarrow nLiH$. The calculated values are 2.06, 3.92, and 6.09 eV for $n = 2-4$, respectively. They showed an almost constant value of around 2 eV for each LiH molecule added to the cluster. Those numbers can be compared with the calculations of Bonacic-Koutecky et al.[16] They found 2.01, 4.05, and 6.05, respectively, in nice agreement with our values. For $n = 4$, the most stable tetrahedral structure has been chosen. The values for the planar structure are 5.62 eV (this work) and 5.79 eV from Bonacic-Koutecky et al.[16]

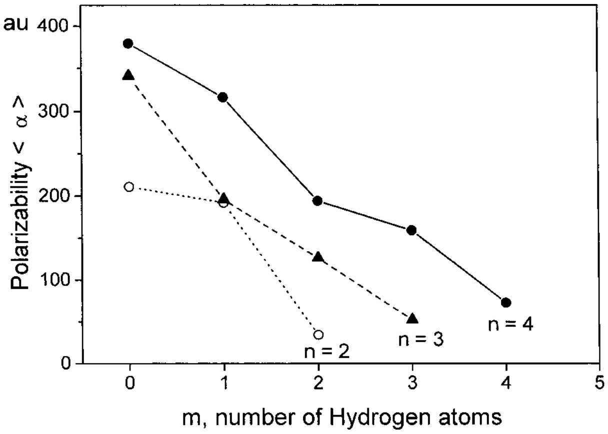

**Figure 2.** Dipole polarizabilities (in au) versus the number of hydrogen atoms in a given cluster. $n$ is the number of lithium atoms.

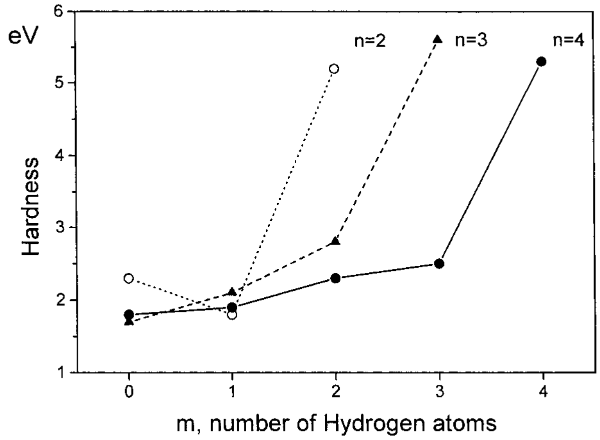

**Figure 3.** Hardness (in eV) versus the number of hydrogen atoms in a given cluster. $n$ is the number of lithium atoms.

In Table 3, the calculated mean polarizability $\langle\alpha\rangle$, anisotropy $\gamma$, and the hardness $\eta$, for all the clusters shown in Figure 1 are displayed. All calculations were done using the 6-311G** basis set. For some of the clusters, calculations were also done using the Sadlej's basis set.[31,32] The results are in parentheses. One can see the small effect of the basis set in the results. The mean polarizability does not change more than 6% in all the studied cases. The hardness does not change in any appreciable amount, and the polarizability anisotropy is the only property that shows a higher sensitivity to the basis set. Whereas for the $Li_4H_2$ isomers and $Li_2H_2$ cluster the anisotropy almost does not change with the basis set, the anisotropy of the $Li_3H_2$ and $Li_3H_3$ clusters shows important changes with the basis set. However, the relative trend of the anisotropy when going from one cluster to another is not affected by variations in the basis set. Hence, one can be confident in the semiquantitative correctness of the calculated values. From the results, the drop in the mean polarizability is evident as more hydrogen atoms are added to a particular cluster. On the contrary, the hardness augments dramatically when the cluster is hydrogen saturated. This is in nice agreement with the rise of the ionization potential described by Rao et al.[15] The polarizability anisotropy is even more sensitive to the amount of hydrogen. It falls sharply as the number of hydrogen atoms augments. This is mainly a symmetry effect. It is very interesting to note that the polarizability as a whole (mean and anisotropy) is able to distinguish between different isomers of a given cluster. For instance, the two studied isomers of $Li_4H_3$ can be clearly separated by looking at the anisotropy. The same is true for the three isomers of $Li_4H_2$.

Figures 2 and 3 show respectively the variation of the mean polarizability and the hardness with respect to the number of hydrogen atoms in the cluster. One can see a decrease in the polarizability with the augment in the number of hydrogen atoms. This effect almost dissappears when a dimension transition occurs; e.g., between $Li_4H_2$ and $Li_4H_3$, the first one is planar, two-dimensional, and the second one is three-dimensional. In these cases, the augment in volume is noticeable and should produce an increase in the polarizability, which is in competition with the electronic effect, thus reducing the polarizability. Figure 3 shows clearly the abrupt rise in the hardness at the saturation level. According to the principle of maximum hardness, this is a clear indication that the hydrogen-saturated clusters are the most stable. The differences with the less saturated clusters is so marked that the experimental observation and characterization of these clusters could be complicated.

## Conclusions

We have calculated the dipole polarizability and the hardness of a series of small lithium clusters doped with hydrogen. The trends have been rationalized in comparison with the ionization potential variations and the postulated metal–insulator transition. The main points in the conclusions below are independent of the number of atoms.

The mean polarizability shows a clear decrease when more hydrogen atoms are added to a given lithium cluster. This is a clear consequence of the metal–insulator transition, and one can predict the same behavior in the dipole polarizability of other ionic mixed clusters such as $Na_nCl_m$.

The hardness variations confirm that the hydrogen-saturated clusters are the most stable and that the experimental observation of the other clusters could be complicated due to their high reactivity.

The various possible isomers of a given cluster, such as the isomers of $Li_4H_4$, $Li_4H_3$ and others, can be identified through the polarizability anisotropy. They present marked differences that cannot be modified by more accurate calculations. In contrast, the mean polarizabilities are very similar and the tendencies could be modified by other effects, like the temperature.

**Acknowledgment.** Part of this work has been supported by FONDECYT (Fondo de Desarrollo Cientifico y Tecnologico), Grant 1981231.

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