Relationship between Ionization Potential, Polarizability, and Softness: A Case Study of Lithium and Sodium Metal Clusters

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The properties of the alkali metal clusters have been investigated by using ab initio electronic structure calculations, with special reference to their structural evolution and the size dependence of several reactivity descriptors, such as ionization potential, electron affinity, polarizability, chemical potential, hardness, softness, etc. Also shown is a good inverse correlation between the dipole polarizability and the ionization potential of the neutral clusters. Similarly, the softness parameter has also been shown to correlate strongly with the dipole polarizability of the clusters. The present work thus will have some important implications in the calculation of polarizability of metal clusters in terms of the corresponding ionization potentials directly.

I. Introduction

The concept of hard−soft acid−base (HSAB), introduced by Pearson, has been quite successful in rationalizing many chemical reactions.[1] The subsequent developments on the quantification of hardness by Parr and Pearson,[2] rationalization of the HSAB principle,[3] the principle of maximum hardness (PMH),[4] and the introduction of various associated local reactivity descriptors (local softness and Fukui function)[5−10] have added further importance to this area of research.[11−18] One of the key aspects in these conceptual developments lies in the fact that the reactivity descriptors might not be experimentally observable quantities and hence further work has often been necessary to explore the possible relationships of these descriptors with suitable observable quantities which can also critically rationalize the quantitative definition of the descriptors. In view of this, several studies have been carried out to show the correlation between the softness of the systems with the polarizability.[10−15] Although the above qualitative relationship appears to be simple for the atomic systems, the extension of these conceptual developments to the molecular systems has been very limited.

Another interesting issue is concerned with the study of the relationship between the important molecular properties, such as the polarizability and the ionization potential (IP). There have been few studies in the literature to establish a relationship between these two quantities.[19−22] The static electric dipole polarizability is a measure of the distortion of the electron density under the effect of an external static electric field. However, the first ionization potential measures the extraction energy of the outermost electron of the atom and thus indirectly reveals how tightly an electron is bound within the nuclear attractive field of the systems. Thus, it has been qualitatively expected that these two parameters should be inversely related to each other. Such a relationship has been first derived by Dmitrieva and Plindov and has been shown to be valid for atomic systems.[22] This approach has provided a route to obtain the polarizability in terms of the other properties rather than through a direct calculation.

While such relationships have been studied for atomic and selected molecular systems with reasonable success,[19−23] they have not been explored in the newly emerging field of metal clusters, which has become an important topic of research due to their unique properties and applicability in different areas such as cluster assembled materials, nanodevices, and catalysis.[24−28] In light of the above discussion, we focus on two systems, namely sodium and lithium clusters (Na_n and Li_n, $n = 1-10$), which serve to illustrate some of the issues discussed above. These clusters have been considered to be one of the prototype systems for the study of the size dependence of geometries, energetics, and structural stability.[26,29] Despite the availability of experimental and theoretical results for these alkali metal clusters, the connection between the size evolutions of their electronic properties is not yet fully understood. Although these two clusters have similar electronic and geometrical structures, their properties at the intermediate cluster sizes are different from each other.[29] We discuss here the properties of metal clusters emphasizing the different aspects pertaining to their structural evolution and the size dependence of several reactivity descriptors, such as IP, electron affinity, polarizability, chemical potential, hardness, softness, etc., and also we explore the relationship between the polarizability, IP, and softness of the Li_n and Na_n clusters.

II. Theoretical Background: Reactivity Descriptors

In density functional theory (DFT), the ground-state energy of an atom or a molecule can be expressed as a functional of its electron density $\rho(\mathbf{r})$ as,[30]

$$E[\rho] = F[\rho] + \int d\mathbf{r}\; v(\mathbf{r})\, \rho(\mathbf{r}) \qquad (1)$$

where $v(\mathbf{r})$ is the external potential that includes the nuclear potential, and $F[\rho]$ is the universal Hohenberg−Kohn functional composed of the electronic kinetic energy and the electron−electron interaction energy. The first and second partial derivatives of $E[\rho]$ with respect to the number of electrons N at

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constant external potential define the chemical potential μ and the global hardness η of the system respectively[2,31,32] as

$$\mu = \left(\frac{\partial E}{\partial N}\right)_{v(\mathbf{r})} \tag{2}$$

$$\eta = \left(\frac{\partial^2 E}{\partial N^2}\right)_{v(\mathbf{r})} \tag{3}$$

The global hardness has been an indicator of overall stability of the system and its inverse defines the global softness as

$$S = 1/2\eta \tag{4}$$

It has been customary to employ a finite difference approximation to the derivatives, using the energies of N, $(N + 1)$, and $(N - 1)$ electron systems, and obtain as operational definitions of μ, η, and S the results[31]

$$\mu \approx -(\mathrm{IP} + \mathrm{EA})/2 \tag{5}$$

$$\eta \approx (\mathrm{IP} - \mathrm{EA})/2 \tag{6}$$

$$S \approx 1/(\mathrm{IP} - \mathrm{EA}) \tag{7}$$

where IP and EA are the first vertical ionization energy and electron affinity of the chemical species, respectively.

III. Computational Details

Second-order Möller−Plesset (MP2) and density functional with B3LYP exchange-correlation calculations have been performed to study the different reactivity descriptors and the relationship between the polarizability, IP, and softness of the lithium and sodium clusters. We have employed split-valence 6-311+G(d) basis sets in this present study. The geometries of all the sodium and lithium clusters were optimized without any symmetry constraints, using B3LYP density functional and the standard split valence basis set, 6-311+G(d). The restricted HF method has been used for the calculation of energy of the neutral systems and for the corresponding anionic and cationic species the restricted open shell HF method has been used. The spin multiplicity corresponding to singlet and doublet has been considered for the even and odd number clusters, respectively. The calculations have been performed with the GAMESS system of programs.[33] We have used the grid based DFT in GAMESS that employs a typical grid quadrature to compute the integrals. During the SCF procedure, the grid consists of 96 radial shells with 36 and 72 angular points.

In general, the static response properties of a molecule can be defined by expanding the field-dependent energy $E(\mathbf{F})$ as a series in the components of a uniform electric field $\mathbf{F}$, viz.,

$$E(\mathbf{F}) = E(0) + \sum_i \mu_i \cdot F_i + {}^1\!/_2 \sum_{i,j} \alpha_{ij} \cdot F_i F_j + ... \tag{8}$$

where $E(0)$ is the energy of the system in the absence of the electric field, μ is the dipole moment, and α is the dipole polarizability tensor. The components of the polarizability tensor are obtained as the second-order derivatives of the energy with respect to the Cartesian components ($i,j = x, y, z$) of the electric field, viz.,

$$\alpha_{ij} = [\mathrm{d}^2E/\mathrm{d}F_i\, \mathrm{d}F_j]_{F=0} \tag{9}$$

The derivatives are evaluated numerically by using the finite field method and the mean polarizability is calculated from the diagonal elements of the polarizability tensor as,

$$\alpha = {}^1\!/_3(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}) \tag{10}$$

IV. Results and Discussions

Before going into the details of the main objectives of the present work (quantitative relationships among various quantities), we first discuss the structure and electronic properties of the alkali metal clusters (Li and Na). The equilibrium geometries of the lithium and sodium clusters obtained by optimization at the level of B3LYP/6-311+G(d) are shown in Figure 1. It is interesting to note that the cluster adopts a different new structure each time when the cluster size is increased by one unit. In general, it is noted that the shape and structure of the Li and Na clusters are very similar to each other. However, it is observed that the average Li−Li bond distance in the lithium clusters is shorter than the Na−Na bond length in sodium clusters. For instance, the Li−Li bond length in Li_2 is 2.709 Å whereas the Na−Na bond length is 3.055 Å, and the corresponding experimental values are 2.673 and 3.08 Å, respectively.[34] A similar trend is observed for other clusters also. There have been studies focusing exclusively on the structure of lithium clusters and it has been shown that there is a geometrical difference between the Li and Na clusters.[35−37] In particular, there is a competition between the planar and nonplanar structures for the clusters of 5 and 6 atoms.[37] The present study, however, shows that the transition from two- to three-dimensional structures of both these clusters starts at the same cluster size of 6.

We now examine the variation of the ionization potential, electron affinity, hardness, and chemical potential parameters with respect to the size evolution of these alkali metal clusters. In general, the chemical potential signifies the direction of electron transfer from one system to another[32] and is equal to the negative of the electronegativity corresponding to the Mulliken's scale.[38] On the other hand, the hardness parameter is interpreted as the resistance of the chemical potential to the change in the number of electrons.[32] It has also been stated that the hardness of a system becomes maximum at the equilibrium nuclear configuration, and hence the stability is directly related to the higher value of hardness.[4] This is known as the principle of maximum hardness.[3] The experimental and theoretical values of the ionization potential and electron affinity of both the clusters are reported in Figure 2 and other related DFT based descriptors, viz., chemical potential, hardness, and softness parameters, are tabulated in Table 1. It can be seen from Figure 2 that the size evolutions of the electronic properties are mostly characterized by the odd−even oscillations and this feature is more prominent for lithium clusters as compared to the sodium clusters. In general, the IPs of lithium clusters are higher than the sodium ones and the trend is reversed for the variation of EA of these two clusters. However, it is found that for the cluster size at 9, the IP of the lithium cluster is smaller than the IP of the sodium cluster. This anomaly is not fully understood.[39] A comparison of the theoretical values of IP for the Li and Na clusters with the corresponding experimental values shows that the values calculated by the MP2 method are better than those with B3LYP method.

The chemical potential and hardness values of the clusters also exhibit the odd−even oscillations, very similar to the size evolution of their IP and EA values. In a recent study, Mineava et al.[17] have also shown such odd−even alternation behavior for the case of sodium clusters. Although the individual values of these parameters, calculated by the MP2 and B3LYP

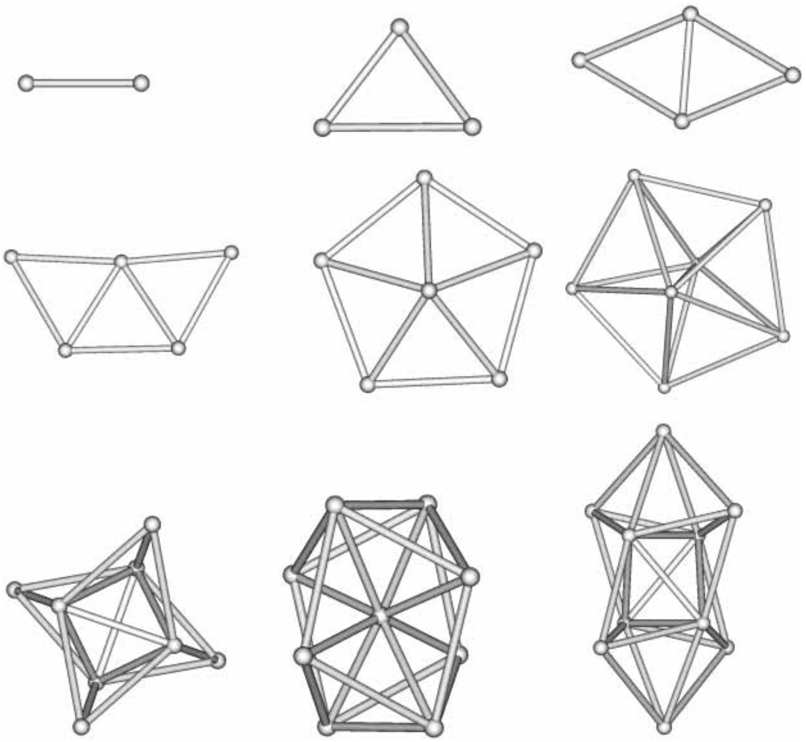

Figure 1. Optimized geometry of lithium and sodium clusters obtained by the B3LYP/6-311+G(d) method.

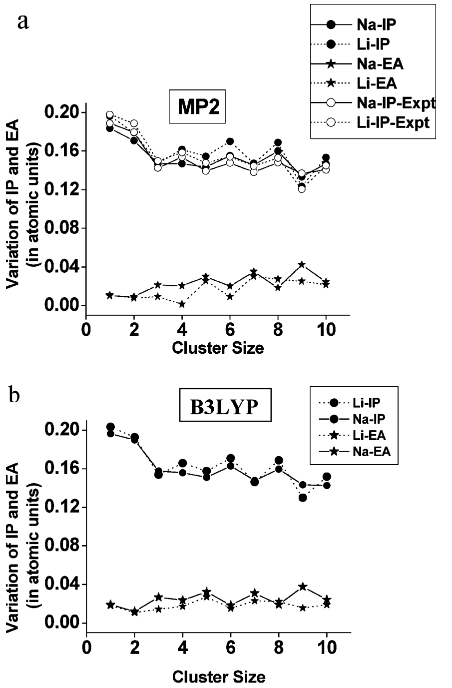

Figure 2. The variation of the ionization potential and electron affinity as a function of the cluster size, calculated by (a) MP2 and (b) B3LYP methods.

methods, show slight deviation from each other, the general trend of variation is similar with minimum values for the chemical potential and EA for the even number clusters. However, the hardness and IP values are high for the even numbered clusters and in particular, their large values for the cluster sizes at 2, 6, and 8 suggest higher stability for these clusters in comparison to the other clusters. It also suggests that the clusters with high ionization potential and low electron affinity are more stable and less reactive. The cluster sizes corresponding to such stability are called magic numbers. The mass abundance spectra of these two sets of clusters have also revealed that the even clusters are more abundant than the neighboring odd ones. The origin of these variations can be explained by closing of the electron shells in the clusters and spin pairing of the electronic levels near the Fermi level. Thus, the chemical potential and hardness parameters also confirm the higher stability of the even numbered clusters and provide physical reasons for the magic properties of these clusters. Although some of the earlier works have attempted to study the variation of these reactivity descriptors and the molecular properties, most of these results are based on the pseudopotential approximation to treat the atomic cores.[9,16] In addition, some of the studies have employed the jellium model approximation and the predicted values underestimated the chemical potential, hardness, and other properties substantially in comparison with the corresponding experimental values. It may be due to the fact that the jellium model does not incorporate the effects of discrete atoms in the clusters.[26,29] The present results, however, are based on the all electron correlated methods and hence are closer to the experimental values also. Very recently, we have reported the effect of electron correlation on the polarizability of the sodium metal clusters and the importance of this effect has been critically analyzed.[40]

Now, turning our attention to the main objective of the present paper, we discuss the relationship between the polarizability, softness, and ionization potential of the lithium and sodium clusters. The individual cluster polarizabilities and the softness values of these clusters of different sizes calculated by the MP2 and B3LYP methods are reported in Table 1. It can be seen that while the atomic polarizabilities of Li (168.52au) and Na (166.88au) are close to each other, as the cluster size grows, the polarizabilities of sodium and lithium clusters differ significantly. It can also be noticed that there is a discrepancy between the experimental and calculated values of the polarizability of the Li and Na clusters, particularly for the higher member Na clusters. The theoretical studies on the polarizability of these clusters with use of very highly sophisticated methods

TABLE 1: Chemical Potential (μ), Hardness (η), Softness, and Polarizability of the Clusters Li_n and Na_n ($n = 1-10$), Calculated by MP2 and B3LYP (DFT) Methods (values in atomic units)

	μ		η		softness		polarizability		
cluster size	MP2	DFT	MP2	DFT	MP2	DFT	MP2	DFT	expt[a,b]
Li1	−0.104	−0.111	0.093	0.093	5.376	5.393	168.52	143.71	163.87
Na1	**−0.098**	**−0.107**	**0.086**	**0.089**	**5.761**	**5.640**	**166.88**	**143.83**	**159.28**
Li2	−0.093	−0.102	0.086	0.091	5.825	5.495	202.77	198.51	221.35
Na2	**−0.090**	**−0.101**	**0.081**	**0.089**	**6.181**	**5.622**	**255.44**	**230.93**	**265.24**
Li3	−0.078	−0.084	0.069	0.070	7.238	7.157	236.20	330.52	232.82
Na3	**−0.084**	**−0.092**	**0.063**	**0.065**	**7.298**	**7.640**	**431.72**	**397.80**	**444.83**
Li4	−0.081	−0.091	0.080	0.074	6.231	6.731	343.67	352.37	326.62
Na4	**−0.083**	**−0.089**	**0.063**	**0.066**	**7.892**	**7.559**	**508.56**	**482.76**	**565.58**
Li5	−0.090	−0.092	0.065	0.065	7.756	7.663	430.76	450.28	428.52
Na5	**−0.086**	**−0.092**	**0.057**	**0.059**	**8.800**	**8.425**	**635.34**	**595.82**	**630.03**
Li6	−0.089	−0.093	0.081	0.078	6.214	6.418	507.05	491.52	360.36
Na6	**−0.088**	**−0.090**	**0.068**	**0.072**	**7.378**	**6.918**	**699.34**	**651.10**	**754.42**
Li7	−0.089	−0.085	0.059	0.062	8.521	8.113	412.08	531.89	538.52
Na7	**−0.090**	**−0.089**	**0.055**	**0.058**	**9.067**	**8.549**	**655.47**	**694.62**	**808.34**
Li8	−0.088	−0.096	0.071	0.073	7.037	6.832	609.17	596.00	561.47
Na8	**−0.089**	**−0.089**	**0.071**	**0.070**	**7.039**	**7.112**	**797.65**	**747.97**	**901.14**
Li9	−0.075	−0.073	0.049	0.057	10.171	8.750	659.31	648.21	601.28
Na9	**−0.087**	**−0.090**	**0.046**	**0.053**	**10.956**	**9.454**	**949.89**	**907.92**	**1062.98**
Li10	−0.087	−0.085	0.066	0.066	7.563	7.530	744.59	715.33	701.83
Na10	**−0.085**	**−0.084**	**0.061**	**0.059**	**8.143**	**8.449**	**1067.96**	**1003.75**	**1309.33**

[a] Reference 43 (for Li clusters). [b] Reference 44 (for Na clusters).

are very scarce in the literature. The recent study of Maroulis[41] on the polarizability for Na and Li atom cases shows that the polarizability values calculated by the finite field coupled cluster method using the large basis sets of near Hartree−Fock quality are much higher than the experimental values. Even for the Li_4 case, it has been shown that the value predicted by the coupled cluster method is much higher than that obtained with the experimental methods.[42] However, we have observed that the prediction made by the MP2 method using the Sadlej basis set is in good agreement with the experimental values.

Analyzing the polarizability trend for the Na and Li clusters, calculated by the MP2 method, reveals that the polarizability values gradually increase from the cluster size 2 to 6, then pass through a minimum at 7, and then increase for other higher clusters. Such minima in the polarizability trend are not exhibited by the B3LYP method, which rather shows that there is a continuous monotonic increase in the polarizability values. This can be attributed to the incorrect asymptotic behavior of the B3LYP functional. The experimental polarizability values as obtained by Benichou and co-workers[43,44] show that the minima is observed only for the Li case at the cluster size of 6 and interestingly no minima is observed for Na clusters. On the other hand, Knight et al. have predicted that the polarizability curve passes through a minimum at the cluster size of 7.[45] More details on the comparison of polarizability values of Na clusters obtained by different theoretical and experimental methods can be found elsewhere.[40]

It is known that the static dipole polarizability is a measure of the distortion of the electronic density and the information about the response of the system under the effect of an external static electric field. However, the ionization potential reveals how tightly an electron is bound within the nuclear attractive field of the systems. Dmitrieva and Plindov were the first to obtain a relationship between the polarizability and the ionization potential for atomic systems using a statistical model.[22] Fricke has shown that polarizability of neutral atoms correlates very well with their first ionization potential (in a logarithmic scale) within the groups of elements with the same angular momentum of the outermost electrons.[20] In a very recent work, Politzer et al. have shown an inverse relationship between α and IP for several neutral atoms with a linear correlation coefficient value of 0.954.[19] In the present work, the relationship between the polarizability α and the IP of the sodium and lithium clusters calculated by the MP2 method is shown in Figure 3, parts a and b, respectively. One can indeed find that there is a good correlation between the cube root of polarizability ($\alpha^{1/3}/n$, where n is the number of atoms present in the cluster) and the inverse of the ionization energy (IP^{-1}/n). The corresponding linear correlation coefficient is found to be 0.999 for the values obtained by the MP2 method. Although we have presented here only the relationship obtained by the MP2 method, the B3LYP method also shows a good linear correlation with a correlation coefficient of 0.995. This is an important observation because the above results can provide a way to calculate the polarizability of the clusters of larger size from the values of their ionization potential. This success in relating the polarizabilities to the ionization potential of these clusters would also be of interest

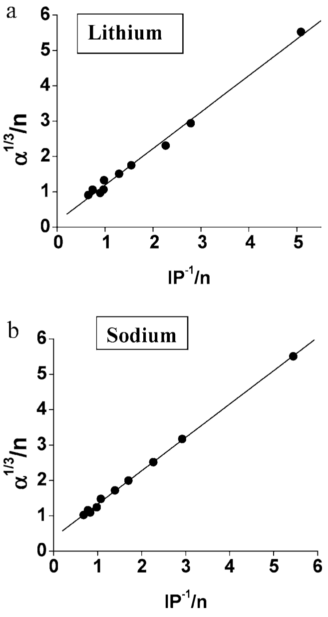

Figure 3. The relationship between the polarizability (α) and ionization potential (IP) of the (a) lithium and (b) sodium clusters calculated by MP2 methods. α and IP values are in atomic units and the factor "n" refers to the number of atoms present in the cluster.

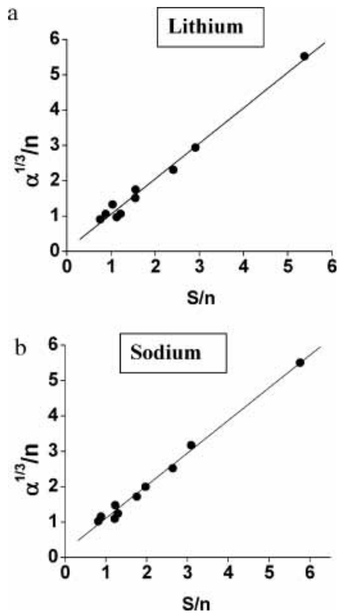

Figure 4. The relationship between the polarizability (α) and softness (S) of the (a) lithium and (b) sodium clusters calculated by MP2 methods. α and S values are in atomic units and the factor "n" refers to the number of atoms present in the cluster.

in relating the local ionization energies with local polarizability, as suggested by Politzer et al.[21]

Now, let us analyze the relationship between the softness and polarizability in these metal clusters. Although the global softness parameter is directly related to the polarizability of the systems, this relation is mostly valid only for atomic systems. It is evident from Figure 4 where the average softness (S/n) of the sodium and lithium clusters is plotted against the average of the cubic root of polarizability ($\alpha^{1/3}/n$) that there exists a linear relation between the two quantities. Both the theoretical methods (B3LYP and MP2) are found to show a very good fit with linear correlation coefficient values of 0.995 and 0.995. It can be noticed from Figure 2 that the electron affinity values of the clusters are much less than that of the ionization potential and hence one can approximate the global softness parameter in terms of the inverse of the ionization potential alone. This may explain the reason the polarizability correlates well with the softness parameter as well as inverse ionization potential.

It is known that the softness of any system, which represents essentially the charge capacity of a species,[46] is expected to be proportional to its size.[13] Similarly, for a sphere of radius R, the polarizability can be approximated as R^3. Hence, it has also been possible to extend a linear relationship between the cubic root of polarizability and the softness from the relationship between the softness and the size of the system. On the basis of the Fermi–Amaldi model, Dmitrieva and Plindov[22] have shown that ionization potential is inversely proportional to the radius of the atomic systems and this relation has further connected the cubic root of polarizability to the inverse of the ionization potential. From the above arguments, the physical basis for the relationship between the cube root of polarizability and the softness as well as the inverse of ionization potential can be rationalized. Herein, we have, however, shown that this relationship can be validated for the metal clusters as well. In addition, a better correlation between these parameters has been observed when these quantities, viz., polarizability, softness, and the inverse of the ionization potential, are divided by the cluster aggregation number (n). The analytical proof of the above relation is, however, yet to be studied for clusters and molecular systems.

V. Concluding Remarks

The size evolution of the chemical potential, hardness, and softness parameters for the lithium and sodium metal clusters is found to show odd–even oscillations, similar to the variation of the ionization potential, electron affinity, and polarizability parameters. The results obtained by B3LYP and MP2 methods reveal that the hardness and IP values are high for the even numbered clusters, particularly for the cluster sizes at 2, 6, and 8, suggesting higher stability for these clusters in comparison to the other clusters. The DFT based descriptors also confirm higher stability of the even numbered clusters and provide the physical reasons for the magic properties of these clusters. The most important new feature of this work, however, lies in the observation that the size-dependent polarizability and ionization potential of the alkali metal clusters very strongly correlate with each other (the linear correlation coefficient is 0.998). We have also found a good linear correlation between the polarizability and softness parameter of the clusters. These results will have some important implications in calculating the polarizability of the systems in terms of the ionization potential directly.

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