# Effect of argon atoms on charge distributions in small lithium clusters

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Charge distributions in lithium clusters $Li_n$ ($n = 3,4,5$) embedded into a matrix of argon atoms have been computed by means of a combined Hartree-Fock and density-functional-theory approach. The positions of the argon atoms, found using molecular-dynamics techniques, points to the origins of pseudo-potential locations. We show that charge alterations in $Li_n$ may be as high as $0.2e$, reflecting local changes in the environment.

## INTRODUCTION

Small clusters of metal atoms have attracted the attention of theoretical and experimental research groups. Many of their more important properties, including cluster stability and reactivity, may be related to the details of their electronic structure. Quantum-mechanical approaches have been widely used in these studies and the results for small lithium clusters have been discussed in numerous publications.[1]

We present a practical approach for the studies of heteroclusters (in this particular application $Li_nAr_m$) with its main emphasis on the smaller of the two subsystems ($Li_n$) embedded in the larger host. We concentrated on modeling the possible changes of the electronic charge distribution in $Li_n$ as caused by an environment of argon atoms; the latter enter into formations with the total potential acting on the $Li_n$ electrons but are not part of the electronic system explicitly treated with the quantum-chemical methods.

Serious problems arise in all attempts to simulate the complicated molecular phenomena of matrix isolation. The present study may also be of interest to the rapidly developing cluster science since, so far, not much attention has been paid to investigations of heteroclusters with theoretical tools.[2,3]

Usually, such studies include Monte Carlo or molecular-dynamics simulations.[4,5] We here also applied the molecular-dynamics technique to study the actual geometry of heteroclusters $Li_nAr_m$ as follows from the solution of the electronic Schrödinger equation for $Li_n$ in an effective field of the argon atoms. Our analysis of the electronic subsystem is entirely based on *ab initio* methods of quantum mechanics and presents a combination of the Hartree-Fock and density-functional theories.

We describe the electron-density distributions in the trapped molecules in terms of conventional quantum-chemical parameters such as partial charges in atoms, orbital population, and related features. Theoretically, an environment of argon atoms should not lead to drastic changes in the electronic properties of molecular systems within cells and so, no considerable changes are expected. However, detecting even small distortions in the charge distribution, due to matrix effects, may have serious consequences for future applications, because it provides evidence of a matrix's effect, for instance, on the reaction dynamics in a trapped system. It is therefore important to learn what the changes in the electronic structure due to a matrix environment can be in order to draw mainly qualitative conclusions.

## DETAILS OF THE CALCULATION

Electronic distributions in lithium clusters are calculated within the natural population analysis[6] of the spinless first-order density matrix $P$ constructed from a basis of atomic orbitals ($\chi_\mu$):

$$P_{\mu\nu} = \sum_i o_i c_{i\mu} c_{i\nu} , \tag{1}$$

where $o_i$ is the occupational number and $c_{i,j}$ the expansion coefficients of the molecular orbitals of a lithium cluster. This procedure[6] determines the electronic configuration and the net charge of each atom in a polyatomic system.

The set of expansion coefficients ($c_{i\mu}$) is obtained from the Roothaan-type equation modified by taking into account the presence of surrounding noble-gas atoms:

$$\sum_\nu \left[ (F + V_{ext})_{\mu\nu} - \lambda_i (S')_{\mu\nu} \right] c_{i\nu} = 0 , \tag{2}$$

where $F$ is the usual Hartree-Fock operator for a metal cluster in the linear combination of atomic orbitals approximation, $V_{ext}$ is the potential of the external field of noble-gas atoms, and $S'$ is the modified overlap matrix.

To estimate the external potential and the orbitals of the host species the calculations on the Ar atom within density-functional-theory methods are performed at the preliminary stages. According to this self-consistent ap-

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proach[7] the Kohn-Sham equation (in atomic units) is

$$[-\tfrac{1}{2}\Delta+\Phi^a(r)+V_{xc}]\psi_j^a(r)=c_j^a\psi_j^a(r) \ , \tag{3}$$

$$\rho^a(r)=\sum_j o_j|\psi_j^a(r)|^2 \ , \tag{4}$$

with the classic electrostatic $[\phi^a(r)]$ and exchange-correlation $[V_{xc}{}^a(r)]$ potentials.

We use the Slater-type dependence for the exchange energy[7] and the Vosko-Wilk-Nisair approximation for correlation energy.[8] For a given basis set $(\xi_\mu)$, the matrix equation[2] in the corresponding matrix form is solved and the potential is

$$V_a^{Ar}(r)=-\left[\frac{Z_{Ar}}{r}\right]e^{-\alpha r^2}+\sum_k d_k e^{-\beta_k r^2} \ , \tag{5}$$

where spherical symmetry is assumed. The coefficients $\alpha$, $\beta_k$, and $d_k$ are obtained by the least-square fit and $Z_{Ar}$ is the nuclear charge of Ar.

The external potential in Eq. (2) is written

$$V_{ext}=\sum_a\left[V_a^{Ar}-\sum_j\epsilon_j^a|\psi_j^a\rangle\langle\psi_j^a|\right] \ , \tag{6}$$

where the sum over $a$ includes all the noble-gas atoms and the sum over $j$ includes occupied atomic states from the solution of Eq. (3) for Ar. The corresponding expression for the overlap operator is as follows:

$$S'=1-\sum_a\sum_j|\psi_j^a\rangle\langle\psi_j^a| \ . \tag{7}$$

The projection operators in Eqs. (6) and (7) preserve the orthogonality of sets of one-particle states for metal cluster and environmental systems, respectively. They play the same role as the corresponding projectors in pseudo-potential theories. Generally, the basis sets $(\chi_\mu)$ for metal atoms and $(\xi_\mu)$ for argon atoms may different.

By using the above formulas, we suggest that the argon eigenstates in the doped cell are essentially the same as those in a isolated atom, which, in particular, prevent a charge transfer between the guest and host subsystems as presented below.

The molecular-dynamics simulation procedure considers the cluster $Li_n$ surrounded by $m$ atoms of Ar by representing at first a few coordination spheres. Interaction energy is written as a sum of pair interactions Ar-Ar and Ar-Li, where the parameters correspond to the Lennard-Jones potential. In nullifying the forces acting on the lithium atoms, fixing the $Li_n$ species, the hetero-cluster $Li_n Ar_m$ is allowed to adjust its own geometry with the help of the steepest descent method.[9] The final positions of the Ar atoms indicate the places where the $V_a^{Ar}$ potentials should be centered.

The geometric configurations of planar $Li_3$, $Li_4$, and $Li_5$ clusters are shown in Fig. 1.[10] These parameters have been inserted in calculations, constituting an additional approximation for the modeling of matrix isolation phenomena. Therefore the matrix will force the flexible species (some of the frequencies of the $Li_n$ clusters are fairly low) to change their geometry. We have checked that the electronic distribution is not susceptible to possible geometric distortions.
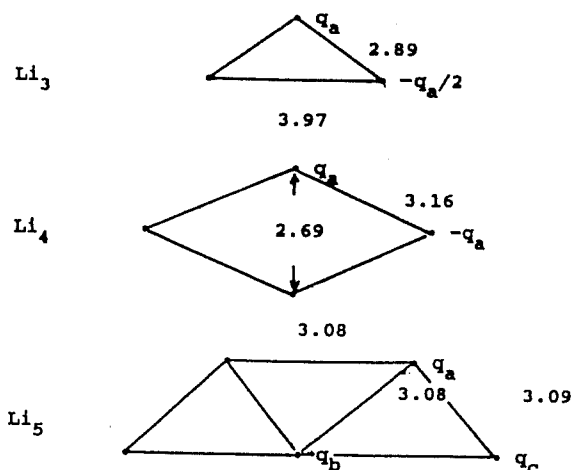


FIG. 1. Geometry of planar lithium clusters (Ref. 10) (distances in Å) and designations of charges ($q_a$, $q_b$, and $q_c$) are the same as in Table I.

The parameters of the Lennard-Jones potential,[11,12]

$$V_{LJ}(r)=C4D\left[\left[\frac{\sigma}{r}\right]^{12}-\left[\frac{\sigma}{r}\right]^6\right] \ , \tag{8}$$

are $D=8.49\times10^{-15}$ erg, $\sigma=4.45$ A for Ar-Li and $D=1.67\times10^{-14}$ erg, $\sigma=3.4$ A for Ar-Ar. However, the Lennard-Jones pair potential does not critically influence the calculated properties of such heteroclusters.[13]

Conventional split-valence 3-21G and 6-31G basis sets of contracted Gaussian functions[14] have been used to transform the electronic equations into matrix form. The Hartree-Fock-Roothaan equations have been solved in the spin-restricted version for $Li_4$ and in the unrestricted version for the open-shell systems $Li_3$ and $Li_5$. Calculations of net charges and effective electronic configurations for lithium atoms have been performed using natural population analysis programs[6] which we modified.
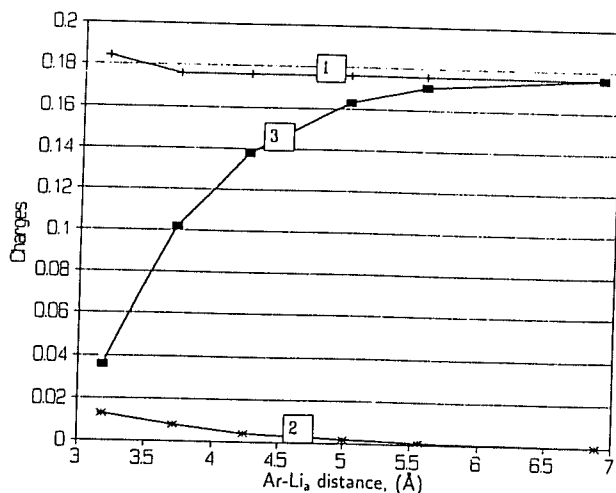


FIG. 2. The net atomic charges computed for the Ar-$Li_3$ cluster. Curves 1 and 2 show the charges on the apex lithium atom $Li_a$ on the closest to argon and on argon, respectively, calculated by the Hartree-Fock wave functions of the entire complex. Curve 3, which should be compared to curve 1, shows the charges on $Li_a$ computed by the proposed technique.

TABLE I. The net charges on atoms in the $Li_3$, $Li_4$, and $Li_5$ clusters (see Fig. 1 for designations). The results are obtained by the Mulliken population analysis and natural population analysis. The results for $Li_n Ar_m$ heteroclusters by the NPA/3-21G approach are also shown.

| Approximation | $Li_3$ $q_a$ | $Li_4$ $q_a$ | $Li_5$ $q_a$ | $q_b$ | $q_c$ |
|---|---|---|---|---|---|
| | Separated lithium clusters | | | | |
| MPA/6-31G | 0.448 | 0.158 | 0.054 | 0.281 | −0.294 |
| MPA/3-21G | 0.396 | 0.236 | 0.104 | 0.327 | −0.268 |
| NPA/6-31G | 0.178 | 0.278 | 0.172 | 0.133 | −0.239 |
| NPA/3-21G | 0.176 | 0.268 | 0.163 | 0.135 | −0.231 |
| | Heteroclusters | | | | |
| $Li_n Ar_m$, large | 0.193 | 0.366 | 0.173 | 0.194 | −0.270 |
| $Li_n Ar_m$, medium | 0.189 | 0.366 | 0.166 | 0.185 | −0.259 |
| $Li_n Ar_m$, small | 0.246 | 0.372 | 0.179 | 0.163 | −0.260 |

## RESULTS AND DISCUSSION

To verify our approach, we calculated the charges in the cluster Ar-$Li_3$ for different distances from Ar to the apex lithium atom, $Li_a$. Figure 2 presents the results for the charges on $Li_a$ (curve 1) and on Ar (curve 2) obtained at the Hartree-Fock level for the entire cluster Ar-$Li_3$. Curve 3 shows the charge on $Li_a$ calculated by the described procedure, namely, treating the $Li_3$ species in the presence of the Ar external potential. Clearly our approximation is justified for the Ar-Li distances which are close to or greater than the equilibrium Ar-Li position of approximately 5 Å.[11] For distances smaller than 4 Å, where the charge transfer to argon becomes noticeable, our pseudopotential approach is inadequate. Fortunate-
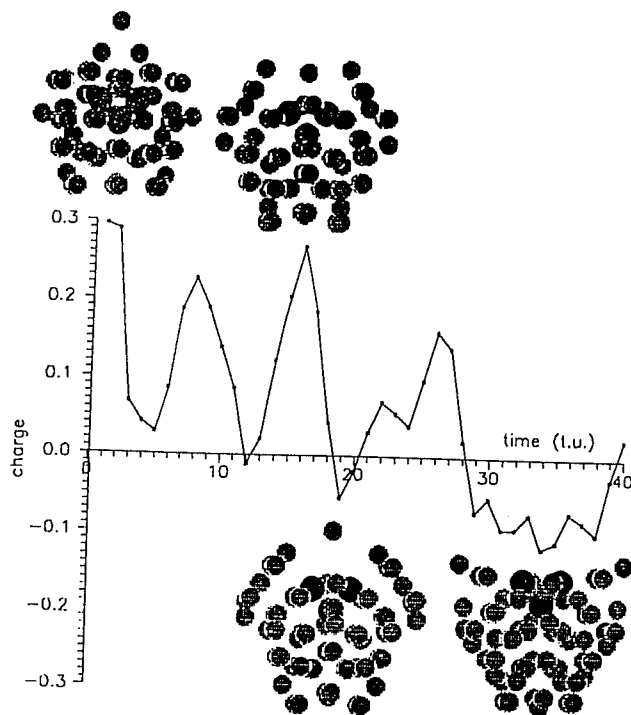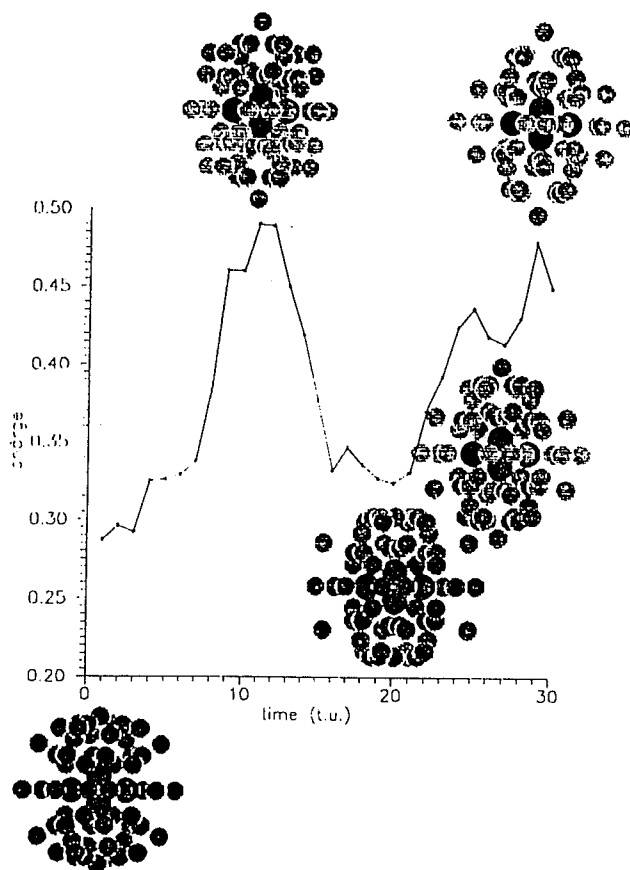


FIG. 4. The temporal evolution of the $Li_4 Ar_{62}$ heterocluster (t.u. equals 2.6 ps.) at $T=2.4$ K. The charges for the apex lithium atom $Li_a$ (see Fig. 1) are also shown.

ly, the closest distances between the Ar and Li atoms found through molecular-dynamics simulations for $Li_n Ar_m$ are greater than 4.34 Å and therefore our scheme provides reasonable estimates for the charges.

Table I contains the computed charges on atoms in $Li_3$, $Li_4$, and $Li_5$ trapped inside the argon cells. For $Li_3$ and $Li_4$ the charges on the atom designated as $Li_a$ in Fig. 1 are sufficient, while the partial charges of the remaining centers are easily deduced from the symmetry.

First of all, we should point out that, as expected, the Mulliken population analysis gives figures essentially dependent on the basis sets (Table I). The natural population analysis (NPA) results from charges considerably more stable with respect to the basis set (third and fourth lines of Table I). The NPA charges obtained with 3.21G basis sets are only later discussed for $Li_n Ar_m$ heteroclusters.

Table I shows the partial charges of lithium clusters within argon cells as well. Initial configurations for the molecular-dynamics problem corresponded to an arrangement of 5 fcc coordination spheres (62 atoms) with the lithium species at the center and the cell parameter (6 Å) slightly exceeding the pure Ar crystal value (5.3 Å). Two external spheres have been fixed and the positions of all particles within them have been, respectively, optimized (the structures indicated as "large" in Table I). The structures called "medium" and "small" have been
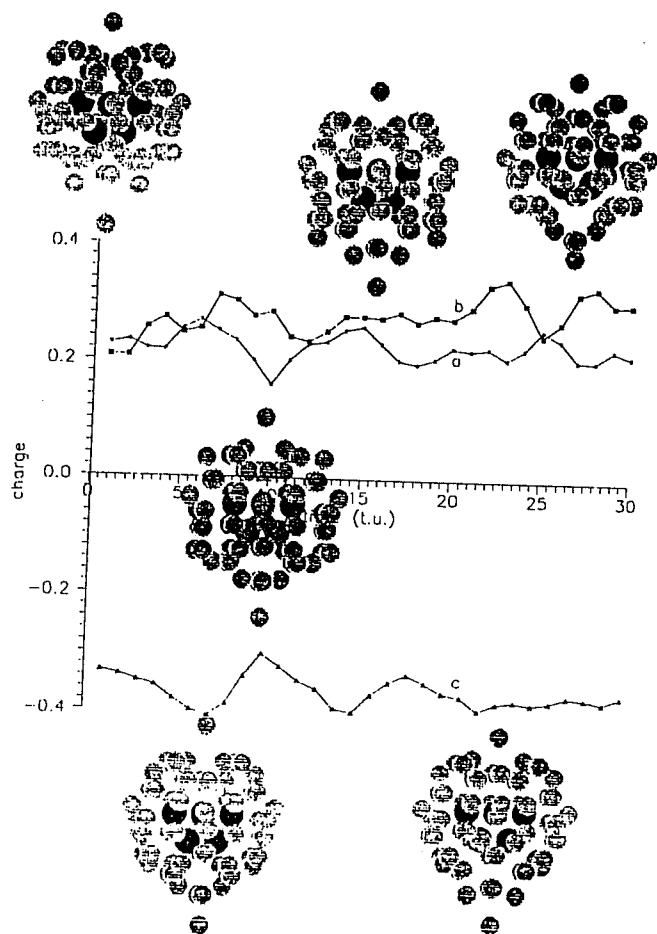


FIG. 3. The temporal evolution of the $Li_3 Ar_{62}$ heterocluster (t.u. equals 2.6 ps.) at $T=35$ K. The charges for the apex lithium atom $Li_a$ (see Fig. 1) are also shown.

FIG. 5. The temporal evolution of the $L_5Ar_{62}$ heterocluster (t.u. equals 2.6 ps.) at $T=18$ K. The charges for the apex lithium atom, $Li_a$ ("$a$"), $Li_b$ ("$b$"), and $Li_c$ ("$c$") (see Fig. 1 for designations), are also shown.

obtained by deleting from the electronic equation (2), the external potentials corresponding to the farthest argon atoms. The medium sets are $Li_3Ar_{41}$, $Li_4Ar_{40}$, and $Li_5Ar_{40}$ while the small sets are $Li_3Ar_{19}$, $Li_4Ar_{22}$, and $Li_5Ar_{18}$.

Comparison of the two parts of Table I shows that an environment of argon can cause small, but noticeable, changes in charge distributions in lithium clusters. The charge shifts range from $0.02e$ to $0.1e$ and these effects may be significant in the study of the mechanisms of matrix reactions of lithium clusters with such polar reagents as $H_2S$.[15] As compared to the chemisorption studies of H atoms on Li crystals with a bcc structure,[16] the charge changes calculated are reliable.

Obviously, the local arrangement of the argon atoms surrounding the metal system plays an essential role in creating the charge shift. Figures 3, 4, and 5, respectively, show the variations of the atomic charges in $Li_3$, $Li_4$, and $Li_5$ species as accompanying variations in heterocluster structures in the course of temporal evolution. The geometric configurations of $Li_nAr_m$, which correspond to some of the extrema in the charge curves, are indicated for convenience. The local charge alterations in $Li_n$ may be as high as $0.2e$ depending on the changes in the environment. This agrees with the results of studies of H absorption on Li crystals.[16]

Though encouraging, these results are not satisfactory. As concerns the modeling of matrix phenomena, the inadequacies, due to the scarcity of argon atoms as well as to the rigidity of the metal clusters entailed in these computations, would need to be improved in the future.

## ACKNOWLEDGMENTS

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