Polarizabilities of Intermediate Sized Lithium Clusters
From Density-Functional Theory

Rajendra R. Zope
Department of Physics, University of Texas El Paso, El Paso TX, 79968, and NSF CREST Center for Nanomaterials Characterization Science and Process Technology, Howard University, School of Engineering, N.W. Washington D.C. 20059

Tunna Baruah
Department of Physics, University of Texas El Paso, El Paso TX 79968

Mark R. Pederson
Center for Computational Materials Science, Code 6392, Naval Research Laboratory, Washington DC 20375

Received 30 May 2007

Abstract:
We present a detailed investigation of static dipole polarizability of lithium clusters containing up to 22 atoms. We first build a database of lithium clusters by optimizing several candidate structures for the ground state geometry for each size. The full polarizability tensor is determined for about 5-6 isomers of each cluster size using the finite-field method. All calculations are performed using large Gaussian basis sets, and within the generalized gradient approximation to the density functional theory, as implemented in the NRLMOL suite of codes. The average polarizability per atom varies from 11 to 9 Å³ within the 8-22 size range and show smoother decrease with increase in cluster size than the experimental values. While the average polarizability exhibits a relatively weak dependence on cluster conformation, significant changes in the degree of anisotropy of the polarizability tensor are observed. Interestingly, in addition to the expected even odd (0 and 1 μB) magnetic states, our results show several cases where clusters with an odd number of Li atoms exhibit elevated spin states (e.g. 3 μB).

Keywords: Density-Functional Theory, NRLMOL, Polarizability, Lithium Clusters

PACS: 32.10.Dk, 33.15.Kr, 42.65 An, 36.40.Cg, 30.40.Vz

Mathematics Subject Classification:

1 Introduction

Materials composed purely of alkali atoms are expected to closely mimic the free-electron gas or jellium models as they have only one very delocalized electron outside of a noble-gas shell. Because of the relative simplicity of pure alkali systems they are often viewed as good systems for

---

1rzope@utep.edu
2tbaruah@utep.edu
3mark.pederson@nrl.navy.mil
4Corresponding author
benchmarking quantum-mechanical methods and for investigating the transition from localized to
inherent electronic behavior [1, 2]. This is especially true for density-functional-based calcula-
tions since the original approximations to density-functional theory [3] were based upon analytical
expressions derived from exchange-only treatments of the free-electron gas. For example Slater
derived an expression for a local potential which reproduced the Hartree-Fock trace of the free
electron gas [4]. Later, Kohn and Sham derived an expression that reproduced the Fermi energy
of the free electron gas [5]. The latter expression also reproduces the total exchange-energy of a
free-electron gas (See for example Ref. [6]). The factor of $3/2$ difference in the Kohn-Sham and
Slater approximations also lead to the use of the $X_{\alpha}$ approximations [4, 7] and approximations
along the lines of this method continue to be investigated as an attractive means for developing
approximate element dependent functionals that permit fully analytic implementation of density
functional theory [8, 9]. Such analytic implementation is computationally very efficient and has
been used for structure optimization of icosahedral fullerenes containing more than two thousand
atoms using triple-zeta quality basis set [10, 11].

The ability to accurately reproduce polarizabilities of large systems is of significant impor-
tance to many forefront research areas in computational chemistry, materials science and quantum
physics. The ability to accurately determine polarizabilities is required to account for hydrogen
bonding, van der Waal’s interactions, [12, 13] solvation effects, [14] and a materials dielectric re-
response. As discussed in Ref. [12], the same interactions or matrix elements required for an accurate
determination of phenomena that are directly mediated by polarizabilities also determine a variety
of transition rates which include spontaneous emission, stimulated absorption and emission, and
Foerster-energy transfer rates. Such rates are of direct importance to the problem of many photovoltaic
applications. The radiative transition rates must also be quantified for applications to quantum-control of matter or any type of light-mediated manipulation of molecular- and cluster-
materials. Derivatives of the polarizability tensor with respect to normal-mode displacement also
determine the intensity of the Raman shifts of a given molecule or cluster [15, 16].

Because of the central role that polarizabilities play in materials science and chemistry there
have been significant efforts aimed at experimentally validating theoretically predicted polarizabil-
ities. However, such experiments are themselves very difficult to interpret for a variety of reasons.
From the standpoint of comparison to experiments on bulk systems, the polarizability of an array
of nonoverlapping polarizable molecules may be approximated from the Clausius-Mossotti rela-
tion. Such comparisons have been performed with some success on very idealized systems such as
fullerene molecules [17, 18, 19, 20]. However, for pure-metal clusters the polarizability may not
be determined from such a means because the individual clusters would coalesce into the the bulk
material if placed upon a lattice. As such the preferred experimental approach for measurement of
metal-cluster polarizabilities rely upon the electrostatic equivalent of a Stern-Gerlach experiment
in which a beam of metal clusters traverse a nonuniform electric field and are deflected due to
the induced polarization of the cluster [21, 22, 23, 24, 25]. Again, for simple systems such a
fullerene molecules quantitative agreement between theory and experiment has been achieved.
However, for metallic clusters deviations exist between different experiments and also between ex-
periment and theory. Generally, it appears that the theoretically predicted polarizabilities display
a more monotonic and smooth behavior than the experimental measurements. Moreover, ear-
lier comparisons suggested that the experimental polarizabilities tended to be larger than theory.
Such discrepancies are now largely understood to be due to temperature dependent corrections
that depend upon the permanent dipole of the clusters. However, some discrepancies still exist
and it is not understood why. One possibility that we attempt to investigate here is that different
low-lying geometries of a cluster may have significantly different polarizabilities or anisotropies in
their polarizabilities.

Experimental measurements of polarizability of Li clusters containing up to 22 atoms have been
reported [25]. Here, we present and compare our density functional predictions of polarizabilities
Polarizabilities of Li Clusters from NRLMOL/DFT

of Li clusters with the available experimental data. The calculations are performed for clusters in the size range 8-22 as number of studies have already addressed polarizabilities up to size 8 \[26, 27, 28\]. Rather than concentrate on the ground state for each size regime we have adopted a different approach that relies on the generation of several low-energy structures. The polarizability of each structure is subsequently calculated to determine whether conformer-induced changes in polarization are expected to be observable.

2 Computational Method

The determination of lowest energy structure of clusters is a nontrivial task. To obtain the candidate structures for the ground state of Li clusters, we make use of a recently determined database of sodium clusters \[29\]. This database is generated using a global optimization technique such as the basin hopping algorithm using the interatomic potential determined within the Kohn-Sham DFT framework. This numerical KS DFT provides very good description of sodium clusters \[30, 31, 32\]. Using starting geometries from this database and Bachelet-Hamman-Schluter pseudo potential method \[33\] we quickly generate low-energy structures for Li clusters using conjugate-gradient technique. A set of few lowest-energy geometries are then selected for further optimization at the all-electron level until forces on all atoms are below the 0.001 Hartree/Bohr. For each of these equilibrium geometries we have then performed six additional calculations with electric fields turned on. The included fields are \((E,0,0), (-E,0,0), (0,E,0), (0,-E,0), (0,0,E)\) and \((0,0,-E)\) with \(E=0.001\) atomic units. From the standard relation between the dipole moment, polarizability, and applied electric field:

\[
p_i = p_i^0 + \sum_j \alpha_{ij} E_j, \tag{1}
\]

we determine the polarizability tensor using a central differencing method. Additional discussion of this procedure may be found in Ref. \[15\]. From the above expression it is possible to determine the central-difference off-diagonal elements \((\alpha_{ij})\) from either \(p_i\) and \(E_j\) or \(p_j\) and \(E_i\). In the limit of a vanishingly small-field or an exactly harmonic polarizability tensor, the values obtained in the two different ways would agree perfectly (regardless of issues related to basis sets). This exact relation provides one way of estimating whether the applied electric field is small enough to accurately determine the polarizability tensor. We find that the off-diagonal elements are small but agree to approximately 1-5%. Of course, the size of the off-diagonal element depends on the original choice of coordinate system. Our original coordinate system uses the principal axes of inertia. To determine the principal polarizability axes we then diagonalize the polarizability tensor and rotate the molecule so that the molecular x, y and z axes coincide with the predicted principle polarizability axes. As a final check we have ascertained for several cases that the predicted polarizabilities are accurate and uncontaminated by higher-order polarizabilities. For these tests, we perform an analysis similar to that of Quong and Pederson for the C\(_{60}\) and Benzene polarizabilities \[18, 19, 20\]. That is, we have determined that the polarizabilities obtained from either energies or dipole moments agree.

To perform the electronic-structure calculations we have used the NRLMOL suite of codes due to Pederson et al. \[34, 35, 36, 37, 38\]. This all-electron method uses Gaussian-type orbitals to represent both the core, valence and unoccupied electrons. A highly accurate variational integration mesh \[34\] is used to calculate matrix elements required for the secular equation. The coulomb potential is calculated analytically (in terms of incomplete gamma functions) \[38\] on this mesh. The exchange-correlation potential and energy kernel is also calculated analytically on this mesh. For the work discussed here we use the Perdew-Burke-Ernzerhof \[39\] generalized gradient approximation. The basis sets here have been specifically optimized for this functional. For Li, we use a total of ten single-gaussians to construct 5 contracted s-type orbitals, 3 contracted p-type orbitals and 1-contracted d-type orbital. Each d-type orbital used also contributes a spherical s-type orbital.
Table 1: Gaussian decay parameter $\alpha$ in bohr$^{-2}$, and contraction coefficients, $c(1s)$ and $c(2s)$, used in this work. As discussed in the text, the default basis set also contains single gaussians. For the $s$ functions we use $\alpha_{8} - \alpha_{10}$. The $p$ functions use $\alpha_{7} - \alpha_{9}$. The $d$ functions use $\alpha_{7}$. For the polarizability calculations, we also include $\alpha_{10}$ and $\alpha_{8}$ for the $p$- and $d$- functions respectively.

| $\alpha$  | $c(1s)$     | $c(2s)$     |
|----------|-------------|-------------|
| 3200.240723 | 0.087121    | -0.015568   |
| 477.961517  | 0.163030    | -0.029089   |
| 108.464722  | 0.278823    | -0.050146   |
| 30.622913   | 0.432000    | -0.078375   |
| 9.925916    | 0.565224    | -0.107102   |
| 3.48695     | 0.560806    | -0.116751   |
| 1.282134    | 0.363596    | -0.098758   |
| 0.466942    | 0.092471    | -0.040081   |
| 0.076048    | 0.001033    | 0.053626    |
| 0.028278    | -0.000155   | 0.028178    |

with an $r^2$ prefactor. This basis set is used for optimizing the geometry. The gaussian exponents ($\beta_i$) used here range between $3.3 \times 10^4$ and 0.028 bohr$^{-2}$. As discussed in detail by Porezag and Pederson, these exponents are optimized iteratively by performing an SCF calculation on the isolated atoms. An application of the Hellmann-Feynman theorem allows us to determine the derivative of the total energy with respect to each decay parameter ($\beta_i$) and then optimize these parameters using the conjugate gradient algorithm. For calculations on Raman spectra and polarizabilities, it is often necessary to include additional polarization functions to account for the response of the electrons to the applied fields. In this work we have included one additional p-type and 1 additional d-type wavefunction. With all of these considerations, the final basis set used for these calculations has 5-s type, 2 $r^2$ s-type, 3x4 p-type, and 5x2 d-type functions or 29 basis functions per atom. The basis sets are displayed in Table 1. Calaminici et al. have suggested that another appealing way of accounting for polarization is to develop functions from the original set that are multiplied by x, y, and z respectively. We have also calculated polarizabilities using this scheme. These are compared with NRLMOL basis set used in present calculations in Table 2. Agreement between two datasets is excellent.

As a final check about the quality of basis set used for description of Li clusters polarizabilities, we calculated the polarizability of Li10-a cluster using very large basis of single optimized gaussians (10 s-type, 10 $r^2$ s-type, 10x3 p-type, and 10x5 d-type or 100 basis functions per atom). This yields an average polarizability of 103.8 Å$^3$ while default NRLMOL basis gives 103.9 Å$^3$. Thus, any uncertainties due to basis sets are quite negligible.

The method used for generating starting geometries and low-energy structures typically leads to many replicas of the lowest energy geometries. Filtering these replicas has been performed in several stages. Each geometry in this work is labeled by the number of atoms (N) and a letter indicating the starting point of the structure. Because of the fact that there are multiple replicas in some cases the letters are not necessarily sequential. Identifying replicated clusters is a difficult task. In this work we have used the principle axes of the polarizability tensor to standardize the coordinate system for each conformer. In addition to being able to compare the values of the polarizabilities, dipole moments and HOMO-LUMO energies, we can view these geometries sequentially which further aids in identifying replicated structures. To more carefully automate this procedure it seems that a vibrational analysis, which includes a secondary inverse-hessian-based quenching to the equilibrium geometry should be performed for each cluster. In addition to
Table 2: Average polarizability ($\AA^3$) of Li clusters using the NRLMOL default basis-sets and a basis-set generated using the augmentation method based on the method of Calaminici et al. Agreement between the two sets is excellent.

| Cluster | NRLMOL | ZC   |
|---------|--------|------|
| Li8-a   | 84.77  | 84.77|
| Li8-b   | 83.31  | 83.3 |
| Li9-a   | 103.15 | 103.14|
| Li9-b   | 96.55  | 96.46|
| Li9-c   | 96.15  | 96.06|
| Li9-d   | 94.26  | 94.14|
| Li9-e   | 93.97  | 93.85|
| Li10-a  | 103.9  | 103.85|
| Li10-b  | 102.84 | 102.78|
| Li10-c  | 104.89 | 104.84|
| Li10-d  | 104.81 | 104.74|
| Li10-e  | 106.93 | 106.87|

being able to compare the infrared and Raman spectra of the clusters, this would lead to a final set of structures with atomic forces that are 10-100 times smaller than those obtained here.

In this work we have allowed for the possibility of spin-polarized solutions. For the clusters containing an even number of electrons we have started the calculations with a net total moment and found that they converge to completely unpolarized solutions. The same thing has been done for the clusters containing an odd number of electrons. In all cases except for one, the odd-atom clusters have converged to structures with a net moment of 1 $\mu_B$ (e.g S=1/2). However, for the 17-atom clusters, we have found that some of the geometries prefer a net moment of 3 $\mu_B$. In this work we have not investigated the possibility of antiferromagnetic spin ordering. Based on what is known about both Li$_2$ dimers and solid lithium, it is unlikely that an antiferromagnetic arrangement of localized spins would be preferred for any of these structures. For example, in Ref. [1] the large-bond length antiferromagnetic state of the Li$_2$ molecule has been investigated within both density-functional theory and self-interaction-corrected density-functional theory using an exchange-only (Kohn-Sham) approximation to the density-functional theory. Both theories correctly reproduce an antiferromagnetic arrangement of spins at very large separations.

3 Results

The optimized structures of the Li clusters in the size range 8-17 are presented in Fig. 1 and 2. Larger clusters are not presented as their structures are too complex to present and are not visually very informative. Primary results of our calculations are presented in Table 3-5 and Figures 3 and 4. With respect to binding energies we find that the binding energy per atom increases slowly and monotonically as a function of cluster size. None of the clusters show uncharacteristically large binding energies in this size regime. The energy gaps, which are often indicators of cluster reactivity and chemical stability, show some reasonably large variations. For example for N=20, all of the clusters have binding energies in the range of 1.16 eV/atom. However, one of the structures has a HOMO-LUMO gap that is 1.5 times larger than the other two structures (Cf. Fig. 4). This is a case where the relative reactivities of the clusters could be the dominant factor in determining which cluster is actually being experimentally observed. However, even for this case the polarizability tensors only differ at the level of a 1-3 percent which is small compared
Figure 1: The structures of lithium clusters in size range 8-11. Note that for a few sizes the labeling is not sequential. (See text for more details).
Figure 2: The structures of lithium clusters in size range 12-16 (See text for more details).
Table 3: Calculated results as a function of cluster size and conformation for N=8 to N=11. Results include moment, µ in Bohr magnetons, binding energy (B.E.) in eV, average and principal polarizabilities (⟨α⟩, α_xx, α_yy, α_zz in Å³), the dipole moment (p_x, p_y, p_z) in atomic units and the HOMO (ε_H), LUMO (ε_L) energies in eV and HOMO-LUMO gap (Δ) in eV respectively. The anisotropy of the polarizability tensor may be determined from the principle polarizabilities (See Eq. 7 Ref. [15]).

| N  | µ  | µ  | B.E. (eV) | ⟨α⟩ | α_xx | α_yy | α_zz | p_x | p_y | p_z | ε_H | ε_L | Δ   |
|----|----|----|----------|-----|------|------|------|-----|-----|-----|------|------|-----|
| 8-a| 0  | -0.94 | 84.77 | 91.88 | 81.31 | 81.12 | 0.01 | 0.00 | 0.00 | -3.09 | -2.24 | 0.84 |
| 8-b| 0  | -0.94 | 83.31 | 89.82 | 80.08 | 80.02 | 0.00 | 0.00 | 0.00 | -3.10 | -2.23 | 0.87 |
| 9-a| 1  | -0.95 | 103.15 | 130.60 | 92.06 | 86.80 | -0.02 | -0.01 | -0.01 | -2.62 | -2.12 | 0.50 |
| 9-b| 1  | -0.95 | 96.55 | 117.00 | 94.60 | 78.04 | 0.00 | 0.00 | 0.00 | -2.57 | -2.27 | 0.30 |
| 9-c| 1  | -0.96 | 96.15 | 109.26 | 82.25 | 81.31 | 0.07 | 0.04 | -0.04 | -2.32 | -1.93 | 0.39 |
| 9-d| 1  | -0.96 | 94.26 | 118.37 | 82.25 | 81.31 | 0.00 | 0.00 | 0.00 | -2.54 | -2.25 | 0.28 |
| 9-e| 1  | -0.96 | 93.97 | 118.36 | 81.85 | 81.70 | 0.00 | 0.00 | 0.00 | -2.33 | -1.93 | 0.39 |
| 10-a| 0  | -0.98 | 103.90 | 140.20 | 89.92 | 81.58 | -0.01 | 0.00 | -0.01 | -2.87 | -2.26 | 0.61 |
| 10-b| 0  | -0.98 | 102.84 | 138.37 | 90.50 | 82.07 | 0.00 | 0.00 | 0.00 | -2.86 | -2.20 | 0.66 |
| 10-c| 0  | -0.98 | 104.89 | 142.08 | 90.50 | 82.07 | 0.00 | 0.00 | 0.00 | -2.85 | -2.19 | 0.66 |
| 10-d| 0  | -0.98 | 104.81 | 142.19 | 90.08 | 82.14 | -0.01 | 0.00 | 0.01 | -2.84 | -2.07 | 0.78 |
| 10-e| 0  | -0.99 | 106.93 | 146.14 | 87.42 | 87.22 | 0.00 | 0.00 | 0.00 | -2.84 | -2.07 | 0.78 |
| 11-a| 1  | -0.97 | 114.89 | 141.63 | 116.78 | 86.25 | -0.01 | 0.00 | 0.01 | -2.91 | -2.53 | 0.38 |
| 11-b| 1  | -0.99 | 117.89 | 160.30 | 106.19 | 87.18 | 0.00 | 0.00 | 0.00 | -2.78 | -2.24 | 0.54 |
| 11-c| 1  | -0.99 | 116.62 | 158.24 | 106.56 | 85.05 | 0.11 | -0.05 | 0.11 | -2.83 | -2.35 | 0.48 |
| 11-d| 1  | -1.00 | 115.46 | 157.40 | 105.70 | 83.26 | 0.00 | 0.00 | 0.00 | -2.87 | -2.38 | 0.50 |
| 11-e| 1  | -1.00 | 115.46 | 157.40 | 105.70 | 83.26 | 0.00 | 0.00 | 0.00 | -2.88 | -2.39 | 0.49 |
| 11-f| 1  | -1.00 | 115.43 | 157.33 | 105.74 | 83.23 | -0.01 | 0.00 | 0.00 | -2.88 | -2.39 | 0.49 |

to the differences between the experimental and theoretical results. The dipole moments are also included in the tables. As expected for a nearly free-electron cluster the dipole moments are nearly negligible. Our data suggests that issues related to dipole moments would be most likely to be important for N=11, N=12, N=16 and N=19. The anisotropy of the dipole moment may be determined from the eigenvalues of the polarizability tensor (labelled α_xx, α_yy, and α_zz in the tables. We emphasize here that these are the eigenvalues of the polarizability tensor and not only the diagonal elements of the polarizability tensor.

Simple models for shell closings in electronic systems have been proposed. These models are often based on jellium descriptions but other potentials such as harmonic-oscillators and central-field models have also been employed to predict shell closings. For the size regimes discussed here, the spherical jellium model would predict shell closings for N=8 and N=20. On the other hand, a central field model would predict shell closing for N=10, N=18 and N=20. The asphericities that appear in the polarizability tensors for the case of N=10 and N=18 argue strongly against an approximate central-field based description of Li clusters in this range. However, for N=20 and N=8 deviations from sphericity are found to be only 2 and 12 percent respectively. The jellium-like behavior is particularly striking at N=20 and departures from sphericity at N=19 and N=21 are also quite pronounced. In comparison to N=19 and N=21 the HOMO-LUMO gap for the N=20 clusters is also large which again indicates a jellium-like behavior has emerged for clusters in this size regime. For most of the clusters studied, the average polarizability did not show significant changes as a function of conformation. However, for N=9 there is a 7 percent variation in average
Table 4: Calculated results as a function of cluster size and conformation for N=12 to N=17. Results include moment, $\mu$ in Bohr magnetons, binding energy (B.E.) in eV, average and principle polarizabilities ($\langle \alpha \rangle$, $\alpha_{xx}$, $\alpha_{yy}$, $\alpha_{zz}$ in $\text{Å}^3$), the dipol moment ($p_x$, $p_y$, $p_z$) in atomic units and the HOMO ($\epsilon_H$) and LUMO ($\epsilon_L$) energies in eV and HOMO-LUMO gap ($\Delta$) in eV respectively. The anisotropy of the polarizability tensor may be determined from the principle polarizabilities (See Eq. 7 Ref. [15]).

| N  | $\mu$ | B.E.  | $\langle \alpha \rangle$ | $\alpha_{xx}$ | $\alpha_{yy}$ | $\alpha_{zz}$ | $p_x$ | $p_y$ | $p_z$ | $\epsilon_H$ | $\epsilon_L$ | $\Delta$ |
|----|-------|-------|--------------------------|--------------|--------------|--------------|------|------|------|----------|----------|-------|
| 12-a| 0     | -1.01 | 123.94                   | 164.68       | 120.32       | 86.82        | -0.01| 0.00 | 0.00 | -2.89    | -2.33    | 0.56  |
| 12-b| 0     | -1.03 | 122.53                   | 162.02       | 118.58       | 86.98        | -0.08| -0.06| 0.04 | -2.88    | -2.34    | 0.54  |
| 12-c| 0     | -1.03 | 122.58                   | 162.11       | 118.54       | 87.09        | -0.10| 0.01 | -0.03| -2.88    | -2.34    | 0.54  |
| 12-d| 0     | -1.03 | 122.47                   | 161.97       | 118.52       | 86.91        | 0.10 | 0.00 | -0.05| -2.88    | -2.34    | 0.54  |
| 12-e| 0     | -1.03 | 122.32                   | 161.73       | 118.13       | 87.11        | 0.10 | -0.03| 0.07 | -2.87    | -2.32    | 0.55  |
| 13-a| 1     | -1.03 | 133.12                   | 171.89       | 129.80       | 97.67        | 0.04 | 0.01 | -0.01| -2.67    | -2.29    | 0.38  |
| 13-b| 1     | -1.04 | 134.47                   | 167.48       | 145.86       | 90.08        | 0.02 | 0.01 | -0.02| -2.78    | -2.29    | 0.49  |
| 13-c| 1     | -1.04 | 133.16                   | 165.51       | 142.63       | 91.34        | 0.01 | 0.00 | 0.01 | -2.83    | -2.41    | 0.43  |
| 14-a| 0     | -1.05 | 142.63                   | 172.56       | 165.80       | 89.53        | 0.00 | 0.00 | 0.00 | -3.02    | -2.18    | 0.84  |
| 14-b| 0     | -1.07 | 142.72                   | 169.07       | 167.87       | 91.22        | 0.08 | 0.01 | 0.08 | -3.03    | -2.24    | 0.78  |
| 14-c| 0     | -1.07 | 142.72                   | 169.07       | 167.87       | 91.22        | 0.08 | 0.01 | 0.08 | -3.02    | -2.24    | 0.79  |
| 15-a| 1     | -1.05 | 153.60                   | 184.89       | 171.97       | 103.94       | -0.06| -0.03| 0.00 | -2.66    | -2.32    | 0.35  |
| 15-b| 1     | -1.07 | 151.09                   | 177.47       | 168.33       | 107.46       | 0.04 | 0.00 | -0.02| -2.77    | -2.36    | 0.41  |
| 15-c| 1     | -1.07 | 151.04                   | 177.12       | 168.36       | 107.63       | -0.04| -0.03| 0.00 | -2.78    | -2.36    | 0.41  |
| 16-a| 0     | -1.08 | 155.31                   | 179.89       | 168.75       | 117.29       | -0.06| -0.02| -0.02| -2.76    | -2.39    | 0.37  |
| 16-b| 0     | -1.08 | 154.75                   | 178.71       | 168.81       | 116.75       | -0.25| 0.20 | -0.30| -2.67    | -2.34    | 0.33  |
| 16-c| 0     | -1.08 | 156.68                   | 180.21       | 171.11       | 118.72       | -0.19| -0.16| 0.04 | -2.65    | -2.42    | 0.23  |
| 16-d| 0     | -1.08 | 154.59                   | 179.97       | 164.62       | 119.20       | -0.31| -0.06| 0.25 | -2.71    | -2.40    | 0.32  |
| 16-e| 0     | -1.09 | 154.46                   | 179.55       | 165.82       | 118.00       | -0.30| -0.03| -0.15| -2.73    | -2.39    | 0.34  |
| 17-a| 3     | -1.11 | 156.15                   | 172.14       | 169.58       | 126.74       | 0.05 | 0.01 | 0.02 | -2.78    | -2.53    | 0.26  |
| 17-b| 3     | -1.11 | 155.86                   | 171.82       | 169.34       | 126.41       | -0.05| -0.04| 0.00 | -2.78    | -2.53    | 0.26  |
| 17-c| 1     | -1.11 | 155.98                   | 172.96       | 170.32       | 124.65       | 0.06 | 0.04 | 0.02 | -2.81    | -2.45    | 0.36  |
| 17-d| 3     | -1.13 | 156.72                   | 171.86       | 149.21       | 149.09       | 0.00 | 0.00 | 0.00 | -2.78    | -2.43    | 0.35  |

polarizability as a function of conformation.

4 Summary and Conclusions

In this paper we have discussed a relatively automated procedure for investigating polarizabilities of clusters as a function of size and conformation. This procedure has been tested on Lithium clusters in the N=8-22 range due to availability of experimental data. While the binding energy per atom and average polarizability show very little nonmonotonic behavior in this range, there are significant departures from isotropic polarizabilities in these clusters. As expected from jellium models it is only for N=20, the polarizability tensor is found to be significantly isotropic. The calculated polarizabilities show smoother decrease with increase in cluster size than the experimental values. The spin polarized calculations indicate that all even size clusters as expected have zero moments (no unpaired electron). However, a few odd size clusters are found to show higher ($3 \mu_{\beta}$) spin states.
Table 5: Calculated results as a function of cluster size and conformation for N=18 to N=22. Results include moment, $\mu$ in Bohr magnetons, binding energy (B.E.) in eV, average and principle polarizabilities ($\langle \alpha \rangle, \alpha_{xx}, \alpha_{yy}, \alpha_{zz}$ in Å$^3$, the dipole moment ($p_x, p_y, p_z$) in atomic units and the HOMO ($\epsilon_H$) and LUMO ($\epsilon_L$) energies in eV and HOMO-LUMO gap ($\Delta$) in eV respectively. The anisotropy of the polarizability tensor may be determined from the principle polarizabilities (See Eq. 7 Ref. [15]).

| N  | $\mu$ | B.E. (eV) | $\langle \alpha \rangle$ | $\alpha_{xx}$ | $\alpha_{yy}$ | $\alpha_{zz}$ | $p_x$  | $p_y$  | $p_z$  | $\epsilon_H$ | $\epsilon_L$ | $\Delta$ |
|----|------|----------|--------------------------|---------------|---------------|---------------|--------|--------|--------|------------|------------|--------|
| 18-a| 0    | 1.12     | 165.36                   | 182.64        | 176.66        | 136.79        | 0.08   | 0.07   | -0.01  | -2.72      | -2.48      | 0.24   |
| 18-d| 0    | 1.11     | 165.82                   | 177.73        | 175.19        | 144.55        | -0.06  | 0.02   | 0.00   | -2.63      | -2.62      | 0.01   |
| 18-e| 0    | 1.11     | 162.84                   | 183.68        | 168.58        | 136.25        | -0.08  | 0.00   | 0.00   | -2.79      | -2.57      | 0.21   |
| 18-f| 0    | 1.10     | 157.79                   | 173.56        | 162.22        | 137.60        | 0.18   | 0.00   | 0.00   | -3.04      | -2.70      | 0.35   |
| 19-a| 1    | 1.14     | 175.95                   | 186.30        | 179.68        | 161.86        | 0.07   | 0.07   | 0.00   | -2.83      | -2.38      | 0.45   |
| 19-c| 1    | 1.12     | 175.25                   | 185.73        | 185.20        | 154.82        | -0.01  | -0.01  | 0.00   | -3.02      | -2.52      | 0.51   |
| 19-d| 1    | 1.12     | 175.43                   | 185.57        | 185.30        | 155.42        | 0.00   | 0.00   | 0.00   | -3.02      | -2.52      | 0.50   |
| 19-e| 1    | 1.11     | 171.09                   | 181.11        | 172.15        | 160.03        | -0.16  | -0.03  | 0.00   | -3.06      | -2.72      | 0.35   |
| 20-a| 0    | 1.16     | 183.22                   | 184.56        | 183.47        | 181.63        | 0.02   | 0.00   | 0.02   | -2.83      | -2.21      | 0.62   |
| 20-b| 0    | 1.16     | 181.62                   | 183.07        | 181.96        | 179.83        | 0.03   | 0.00   | 0.02   | -2.83      | -2.21      | 0.62   |
| 20-c| 0    | 1.16     | 182.82                   | 184.71        | 184.52        | 179.23        | 0.00   | 0.00   | 0.00   | -2.99      | -2.10      | 0.89   |
| 20-d| 0    | 1.16     | 181.17                   | 182.79        | 181.62        | 179.11        | 0.04   | 0.02   | -0.03  | -2.83      | -2.20      | 0.63   |
| 21-a| 1    | 1.16     | 189.70                   | 210.47        | 179.49        | 179.13        | 0.00   | 0.00   | 0.00   | -2.68      | -2.39      | 0.28   |
| 21-d| 1    | 1.16     | 192.43                   | 214.14        | 182.04        | 181.13        | -0.07  | 0.00   | 0.01   | -2.59      | -2.25      | 0.34   |
| 21-f| 1    | 1.16     | 193.01                   | 211.57        | 185.58        | 181.89        | 0.03   | 0.00   | 0.00   | -2.62      | -2.31      | 0.31   |
| 22-a| 0    | 1.16     | 204.14                   | 245.17        | 183.83        | 183.44        | 0.00   | 0.00   | 0.00   | -2.78      | -2.41      | 0.37   |
| 22-b| 0    | 1.16     | 202.98                   | 243.81        | 184.15        | 180.99        | 0.03   | 0.00   | 0.00   | -2.77      | -2.38      | 0.40   |
| 22-c| 0    | 1.15     | 207.80                   | 252.69        | 184.72        | 184.98        | 0.01   | 0.00   | 0.00   | -2.76      | -2.42      | 0.35   |
| 22-g| 0    | 1.15     | 205.79                   | 252.25        | 183.53        | 181.61        | -0.07  | -0.01  | -0.01  | -2.77      | -2.40      | 0.37   |
| 22-h| 0    | 1.15     | 207.67                   | 253.03        | 185.31        | 184.66        | 0.00   | 0.00   | 0.00   | -2.76      | -2.42      | 0.34   |

Figure 3: (Color online) Static dipole polarizability per atom (Å$^3$) of lithium clusters as a function of number of constituent atoms. The polarizability is presented for a number of isomers for each size. The squares represent experimental values.
Figure 4: The HOMO-LUMO gap (eV) of lithium clusters as a function of number of constituent atoms.

5 Acknowledgements

We thank Dr. P. Calaminici and Dr. G. Maroulis for encouraging us to complete the present work for this issue. This work is supported in part by the National Science Foundation through CREST grant, by the University of Texas at El Paso (UTEP startup funds) and in part by the Office of Naval Research, directly (ONR 05PR07548-00) and through the Naval Research Laboratory. Computational support was provided by the DoD High Performance Computing Modernization Office.

References

[1] M. R. Pederson, R. A. Heaton and C. C. Lin, Density-Functional Theory with Self-Interaction Correction: application to the Lithium molecule J. Chem. Phys. 82, 2688 (1985).

[2] M. R. Pederson, J. G. Harrison and B. M. Klein, Studies of Large Lithium Clusters and Their Vacancies with Highly Optimized Localized Orbitals, Mat. Res. Soc. Symp. Proc. 141, 153 (1989).

[3] P. Hohenberg and W. Kohn, Inhomogenous electron gas, Phys. Rev. 136, B864 (1964).

[4] J.C. Slater, A Simplification of the Hartree-Fock Method, Phys. Rev. 81, 385 (1950).

[5] W. Kohn and L.J. Sham, Self-consistent equations including exchange and correlation effects, Phys. Rev. 140, A1133 (1965).

[6] M. R. Pederson, R. A. Heaton, J. G. Harrison and C. C. Lin, Metallic State of the Free-Electron Gas Within the Self-Interaction-Corrected Local-Spin-Density Approximation, Phys. Rev. B 39, 1581 (1989).

[7] J.C. Slater, The Self-Consistent Field for Molecules and Solids, (McGraw-Hill, New York, 1974).

[8] R. R. Zope and B. I. Dunlap, Accurate molecular energies by extrapolation of atomic energies using an analytic quantum mechanical model, Phys. Rev. B, 71, 193104 (2005).
[9] R. R. Zope and B. I. Dunlap, The limitations of Slater’s element-dependent exchange functional from analytic density-functional theory, *J. Chem. Phys.* **124**, 044107 (2006).

[10] R. R. Zope and B. I. Dunlap, Fully analytic implementation of density functional theory for efficient calculations on large molecules, arXiv:cond-mat/0610060v1.

[11] B. I. Dunlap and R. R. Zope, Efficient quantum-chemical geometry optimization and the structure of large icosahedral fullerenes *Chem. Phys. Lett.* **422**, 451 (2006).

[12] M.R. Pederson and T. Baruah, Molecular Polarizabilities from Density-Functional Theory: From Small Molecules to Light-Harvesting Complexes, in *Lecture Series on Computer and Computational Sciences*, Vol 3 pp 156-167 (2005).

[13] K. Park, M.R. Pederson and A.Y. Liu, Vibrational and Electronic Contributions to the vdW Interaction, *Phys. Rev. B* **73** 205116, (2006).

[14] T. Baruah and M.R. Pederson, Density functional study on a light-harvesting carotenoid-porphyrin-C60 molecular triad, *J. Chem. Phys.* **125** , 164706 (2006).

[15] D. V. Porezag and M. R. Pederson, Raman and IR Intensities: A Density-Functional Study *Phys. Rev. B* **54**, 7830 (1996).

[16] R. R. Zope, T. Baruah, M.R. Pederson and B.I. Dunlap, Electronic structure, vibrational stability, infrared and Raman Spectrs of B_{24}N_{24} cages, *Chem. Phys. Lett.* **393**, 300 (2004).

[17] M.R. Pederson, T. Baruah, P. B. Allen and C. Schmidt, Density-functional-based determination of vibrational polarizabilities in molecules within the double-harmonic approximation: Derivation and Application, *J. Chem. Theory and Comp.* **4**, 590 (2005).

[18] M. R. Pederson and A. A. Quong, Charge States, Vibrational Modes and Polarizabilities of Isolated Fullerene Molecules, *Phys. Rev. B* **46**, 12906 (1992).

[19] A.A. Quong and M. R. Pederson, Density-Functional-Based Linear and Non-Linear Polarizabilities of Fullerene and Benzene Molecules, *Phys. Rev. B* **46**, 13584 (1992).

[20] M. R. Pederson, A. A. Quong, J. Q. Broughton, and J. L. Feldman, Fullerene Molecules and Tubules: Polarizabilities, Vibrational Modes and Nanocapillarity, *Comp. Mat. Sci.* **2**, 1994.

[21] K. D. Bonin and V. V. Kresin, Electric-Dipole Polarizabilities of Atoms, Molecules and Clusters, (World Scientific, Singapore, 1997).

[22] W. A. de Heer, The physics of simple metal clusters: experimental aspects and simple models, *Rev. Mod. Phys.* **65**, 611 (1993).

[23] G. Tikhonov, V. Kasperovich, K. Wong, and V. V. Kresin, A measurement of the polarizability of sodium clusters, *Physical Review A* **64**, 063202 (2001).

[24] M. K. Beyer and M. B. Knickelbein, Electric deflection studies of rhodium clusters, *J. Chem. Phys.* **126**, 104301 (2007).

[25] E. Benichou, R. Antoine, D. Rayane, B. Vezin, F. W. Dalby, Ph. Dugourd, M. Broyer C. Ristori, F. Chandezon, B. A. Huber, J. C. Rocco, S. A. Blundell, and C. Guet, Measurement of static electric dipole polarizabilities of lithium clusters: Consistency with measured dynamic polarizabilities, *Phys. Rev. A* **59**, R1 (1999).
[26] G. Maroulis and D. Xenides, Enhanced Linear and Nonlinear Polarizabilities for the Li4 Cluster. How Satisfactory Is the Agreement between Theory and Experiment for the Static Dipole Polarizability? J. Phys. Chem. A 103, 4590 (1999).

[27] M. Pecul, M. Jaszunski, P. Jorgensen, Singlet excitations and dipole polarizabilities of Li2, Li4 and Li8 clusters, Mol. Phys. 98, 1455 (2000).

[28] K. R. S. Chandrakumar, T. K. Ghanty, S. K. Ghosh Ab initio studies on the polarizability of lithium clusters: Some unusual results, Int. J. Quant. Chem. 105, 166 (2005).

[29] S. A. Blundell and R. R. Zope, Structures of sodium clusters by basin hopping algorithm with interatomic potential from the Kohn-Sham density functional theory (unpublished).

[30] S. A. Blundell, C. Guet, and R. R. Zope, Temperature Dependence of the Polarizability of Sodium Clusters, Phys. Rev. Lett. 84, 4826 (2000).

[31] P. Blaise, S. A. Blundell, C. Guet, and R. R. Zope, Charge-Induced Fragmentation of Sodium Clusters, Phys. Rev. Lett. 87, 063401 (2001).

[32] A. Vichare, D. G. Kanehre, and S. A. Blundell, Model dependence of the thermodynamic properties of Na8 and Na20 clusters studied with ab initio electronic structure methods, Phys. Rev. B 64, 045408 (2001).

[33] G. B. Bachelet, D. R. Hamann, and M. Schlüter, Pseudopotentials that work: From H to Pu, Phys. Rev. B 26, 4199 (1982).

[34] M. R. Pederson and K. A. Jackson, Variational Mesh for Quantum-Mechanical Simulations, Phys. Rev. B 41, 7453 (1990).

[35] K. A. Jackson and M. R. Pederson, Accurate Forces in a Local-Orbital Approach to the Local Density Approximation, Phys. Rev. B 42, 3276, (1990).

[36] M. R. Pederson and K. A. Jackson, Pseudo-energies for Simulations on Metallic Systems, Phys. Rev. B 42, 7312, (1991).

[37] D. V. Porezag and M. R. Pederson, Optimization of Gaussian-Basis Sets for Density Functional Calculations, Phys. Rev. A 60, 2840 (1999).

[38] M.R. Pederson, D.V. Porezag, J. Kortus and D. Patton, Strategies for massively parallel local-orbital-based electronic structure calculations, Phys. Stat. Solidi B 217, 187-218 (2000).

[39] J. Perdew, K. Burke and M. Ernzerhof, Generalized Gradient Approximation Made Simple, Phys. Rev. Lett. 77, 3865 (1996).

[40] P. Calaminici, K. Jug, A. M. Koster, Density Functional Calculations of Molecular Polarizabilities and Hyperpolarizabilities, J. Chem. Phys. 109, 07756 (1998).

[41] P. Calaminici, K. Jug, A. M. Koster, Static Polarizabilities of Na_n (for n ≤ 9) Clusters: An all-electron Density Functional Study, J. Chem. Phys., 111, 4613 (1999).

[42] P. Calaminici, A. M. Koster, A. Vela, and K. Jug, Comparison of static polarizabilities of Cu_n, Na_n, and Li_n (n ≤ 9) clusters, J. Chem. Phys. 113, 2199 (2000).