

Theory of Optical Absorption in Lithium Cationic Clusters

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Abstract—Multi-reference singles-doubles configuration-interaction (MRSDCI) approach has been used to calculate the optical properties of small Lithium cationic clusters. This theoretical study has been done to identify their geometrical properties as well as electronic structures. Here I have tried to investigate the linear optical absorption spectra of some simple atomic Lithium cationic clusters' structures with the aim of examining the role of geometry on the optical properties of clusters. Fully *ab initio* electron-electron correlated based approach was employed, and large-scale configuration interaction (CI) calculations were performed to account for the electron-electron correlation effects.

1. INTRODUCTION

Today, there are many types of clusters, such as metallic clusters, organic clusters, semiconductor clusters, molecular clusters etc. All types of clusters have their own features and properties. Recently, the atomic clusters have become hot field of research. This is so because the physics of clusters is connected with the fact that the cluster properties are able to explain the transition from single atom or molecule to the solid state. And so, in the recent years, the study of alkali metal atomic clusters has attracted considerable attention (especially from theoretician) due to small number of electrons involved in their stable structures. Some of these works include the geometry optimizations and energies-calculations by Rao and Jena [1, 2], the MRSDCI scaled geometries and energies calculations by Bonacic-Koutecky *et al.* [3-5] and the comparative study by Rousseau and Marx[6]. At first, Wu experimentally observed the lithium clusters (except Lithium dimer) in the mid 1970s, with the first identification of gaseous Li_3 [7]. Latter on Li_4 was also experimentally observed by him in 1983 [8]. Also, other different aspects of small metal clusters have been studied experimentally [9-11] and theoretically [12, 13].

In the Periodic table of the Elements, Lithium is the first metallic element whose atom has a core consisting of two 1s electrons. It is not possible for 2s valence electron of Li atom to have deep penetration in the core region due to Pauli Principle [14]. Thus, Lithium may be thought as an ideal system for simple metals and Li clusters can be considered a suitable model for studying many fundamental physical

properties of metallic clusters. It is very interesting to explore how the optical spectrum of a Li clusters evolve with the change of geometry of isomers as well as the change in number of atoms of the clusters. The difference in energies of the different structural isomers can be calculated and thus the structural ground state of a cluster can be identified. However this may not be sufficient without experimental benchmarking. The structural and electronic properties of lithium clusters are not directly accessible in experiments. Other indirect observables such as photoabsorption spectra of a cluster can be obtained through experimental measurements which can be interpreted in terms of surface plasma resonance (collective dipole oscillations).

When a cluster is exposed to a perturbing external electric field, the perturbation energy is absorbed and at first, the electrons from the lowest energy states get excited to the higher states which again return to the ground state in a very short period of time. A certain amount of energy is released during this transient time. This released energy is the characteristic of a certain cluster. Thus the photoabsorption of a certain cluster determines the capability to absorb the excitation energy and will be taken as the fingerprint of the cluster. The photoabsorption spectrum strongly depends on the geometry and size of the clusters. The computed theoretical spectra can be compared with the experimentally observed ones. This comparison may serve as a powerful tool to confirm the structure and electronic properties of the clusters.

In this paper, we performed a systematic calculation for optical absorption spectra of various isomers of small cation clusters Li_n^+ ($n = 3, 5$). We analyzed our calculated optical absorption spectra by comparing with the experimental results whichever available. We also tried to investigate how the absorption spectra are affected with the increase of atoms in clusters. Rest of the paper is organized with a brief theoretical background, calculations and results followed by the conclusion.

Theoretical Background

The correlated calculations are performed using the multi-reference singles-doubles configuration-interaction (MRS-

DCI) approach as implemented in the computer program MELD[21]. MRSDCI approach is a well-established quantum-chemical approach in which one considers singly- and doubly-excited configurations from a number of reference configurations, leading to a good treatment of electron correlations both for the ground and the excited states, in the same calculations. Using the ground- and excited-state wave functions obtained from the MRSDCI calculations, electric dipole matrix elements are computed and subsequently utilized to compute the linear absorption spectrum assuming a Lorentzian line shape. By analyzing the wave functions of the excited states contributing to the peaks of the computed spectrum obtained from a given calculation, bigger MRSDCI calculations are performed by including a larger number of reference states. The choice of the reference states to be included in a given calculation is based upon the magnitude of their contribution to the CI wave function of the excited state (or states) contributing to a peak in the spectrum. This procedure is repeated until the computed spectrum converges within an acceptable tolerance, and all the configurations contributing significantly to various excited states are included in the list of the reference states. In the past, my group has used such an iterative MRSDCI approach on a number of conjugated polymers to perform large-scale correlated calculations of their linear and nonlinear optical properties [15-21], and also for small boron and aluminum clusters [22-24].

2. CALCULATIONS AND RESULTS

Because finite basis set is employed in electronic structure calculations, it is but natural that the results will depend upon the quality and the size of the basis set employed. Therefore, before comparing our results with the experiments, we want to explore the dependence of photo-absorption spectra on the basis set employing the basis sets 6-311++G(3df,3pd) (excluding the only present last f-function) as well as correlation-consistent basis sets aug-cc-pcVDZ both taken from the EMSL Gaussian Basis Set Library [25, 26].

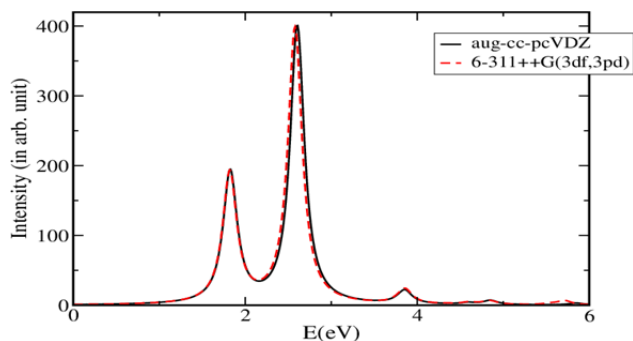


Fig. 1: Optical absorption in Li₂ calculated using different gaussian contracted basis sets.

Upon examining the calculated spectra of Li₂ presented in Fig. 1, the following trends emerge: the spectra computed by augmented basis sets 6-311++G(3df,3pd) and aug-cc-pcVDZ

are in very good agreement with each other in the energy range examined.

Considering good agreement among both the basis sets, I choose to perform calculations for all the isomers of lithium clusters using the basis set 6-311++G(3df,3pd), (excluding the only present last f-function), so as to keep the required computational effort feasible.

It is a well-known fact that the computational effort in a CI calculation performed using N Molecular Orbitals (MOs) scales as $\approx N^6$, which can become quite unfavorable for large values of N . For first principles calculations utilizing large basis sets, generally N tends to be large, and, therefore, it is very important to reduce the number of MOs used in the CI calculations. The number of occupied MOs is reduced by employing the so-called “frozen-core approximation” discussed earlier, while the number of unoccupied (virtual) states are truncated by ignoring high-energy MOs lying far from the Fermi level. The influence of freezing the core orbitals on the optical absorption spectrum of Li₂ cluster is displayed in Fig. 2. It is obvious from the Fig. that it virtually makes no difference to the computed spectra when the core orbitals are frozen. The effect of removing the high-energy virtual orbitals on the absorption spectrum of cluster Li₄ is examined in Fig. 4. From these figures it is obvious that if the virtual orbitals above the energy of 0.8 Hartree are removed from the list of active orbitals, the absorption spectrum stays unchanged. This is understandable on physical grounds because we are interested in computed absorption spectrum in the energy range much lower than 1 Hartree. Therefore, in rest of the calculations, all the 1s core orbitals were frozen, and virtual orbitals with energies larger than this cut off were not considered.

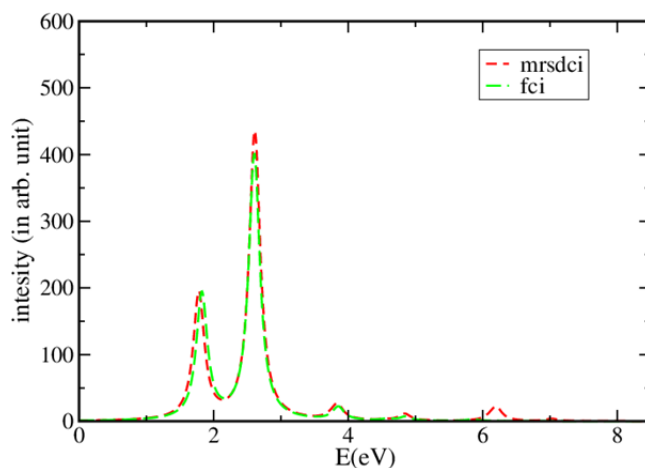


Fig. 2: (Color online) Comparison of optical absorption spectrum of Li₂ computed using the frozen-core approximation (in yellow) as well as at MRSDCI level (in red). Hardly any difference is visible among the two spectra.

In CI calculations, greater numerical accuracy demands the inclusion of a rather large number of configurations which can make the calculations numerically intractable. However, when

it comes to the computation of optical properties, our focus is on calculating accurate energy differences between the ground state, and the excited states, rather than their absolute energies, which is possible even with moderately large CI expansions.

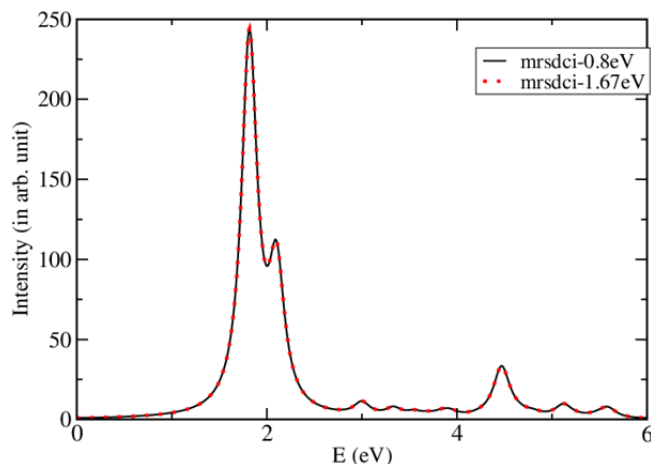


Fig. 3: (Color online) A comparison of optical absorption spectra for excited state of rhombus Li_4 atomic cluster at two different cut-off energies, 0.8 eV (in black) and 1.67 eV (in red). The differences between two sets of calculations are insignificant.

In Table 1 we present the average total number of configurations (N_{total}) for different isomers, with the average computed across different irreducible representations in these symmetry adapted calculations. The fact that these calculations employ close to one million configurations for the cluster considered, makes us confident that our results are fairly accurate. Before we discuss the absorption spectrum for each isomer, we present the ground state energies along with the relative energies of each isomer in Table 2. From the results it is obvious that for Li_5^+ cluster the nonplanar structure is more favorable.

Table 1: Average number of total configurations (N_{total}) involved in CI calculations of various isomers of lithium clusters.

Cluster	Isomer	CI method	N_{total}
Li_3^+	Triangular	FCI	5253
Li_5^+	Planar	MRSDCI	268120
Li_5^+	Non-planar	MRSDCI	400851

Table 2: Ground state (GS) energies (in Hartree) at FCI/MRSDCI level and the relative energies (in eV) of different isomers of clusters.

Cluster	Isomer	CI method	GS energy (Ha)	Relative energy (eV)
Li_3^+	Triangular	FCI	-22.2039	-
Li_5^+	Planar	MRSDCI	-37.1407	0.019
Li_5^+	Non-planar	MRSDCI	-37.1414	0.000

Optical absorption spectra of Li_3^+ cluster

We optimized the geometry of closed shell Lithium trimer (singlet). Firstly, We optimized it at frozen core single double CI (SDCI) level with the Gaussian basis set 6-311++G(3df,3pd) which gave the equilibrium bond length 2.98 Å. To confirm it we further optimized it at MRSDCI level with the the same basis set which showed that although the equilibrium energy lowered down but the bond length remained unchanged. We computed the absorption spectra at frozen core FCI as well as MRSDCI both level with only 55 relevant active virtual orbitals. As shown in Fig. 10 both have the complete agreement. There were observed two strong absorptions, one at 2.70 eV and the other 3.30 eV.

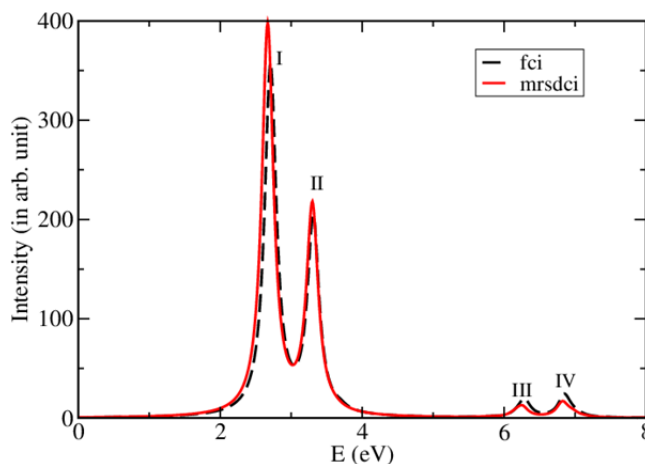


Fig. 4: Optical absorption spectra of Li_3^+ atomic clusters

Optical absorption spectra of Li_5^+ cluster

Here we have taken two different types of clusters with the geometry reported by Ruben O. Weht *et al.* [36] and computed the optical absorption. In planar structure all the atoms are in same plane while in non-planar structure the two triangles are in normal planes. The absorption spectrum for planar cluster is shown in fig. 5 while for non-planar in fig. 6. For planar isomer the strong absorption peaks are observed at 2.35, 2.75 and 3.35 eV. The first peak is dominated by the singly-degenerate transition $H \rightarrow L + 1$. For non-planar isomer the prominent peaks are observed at 1.85, 2.36 and 2.94 eV. The first peak gets the contribution mainly from $H \rightarrow L + 1$. Although the profiles have almost the same pattern for the structures but for the planar one the absorption starts at lower energy.

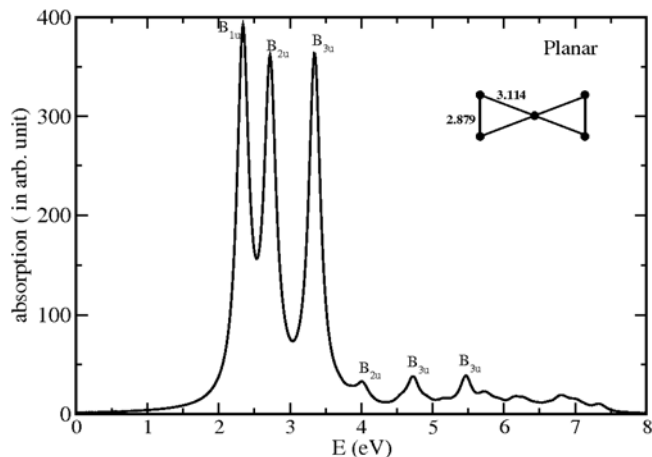


Fig. 5: Optical absorption spectra of Li_5^+ planar atomic clusters at cut-off energy 0.8 eV.

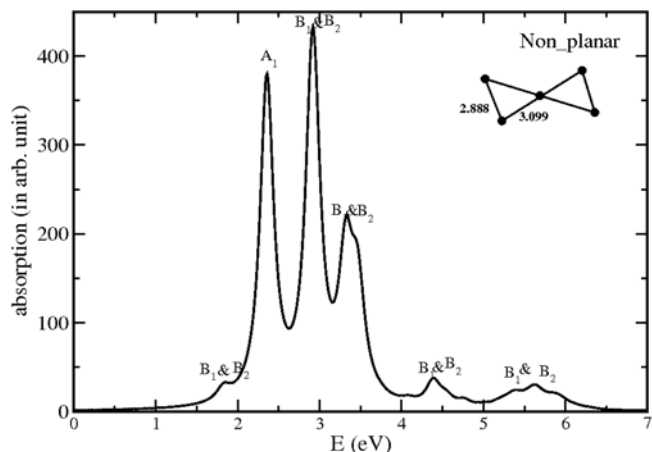


Fig. 6: Optical absorption spectra of Li_5^+ non-planar atomic clusters at cut-off energy 0.8 eV.

3. CONCLUSION

To summarize, the optical absorption study of small lithium cationic clusters were investigated. The electron-electron correlation effect was introduced through configuration method to improve the convergence of result over mean field Hartree-Fock hamiltonian.

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