

# Lithium-oxygen charge transfer interaction: a deformation density analysis study

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## Abstract

Lithium and oxygen interaction plays a cornerstone role in lithium ion and lithium air batteries and lithium based technologies. In this way, oxidation and reduction of neutral and charged lithium is the key process in its application as power source and sustainable energies. Since both oxidation and reduction are based on charge transfer in molecular scale, they can be analyzed via electronic structure changes. Two types of fragmentations for charged complexes were suggested, in which the positive charge was located on either lithium or oxygen fragment. Deformation density analysis is a recently developed technique for identification of different intermolecular interactions in the context of quantum chemical language. In this analysis, the molecular orbitals of isolated fragments were employed to build non-interacting and anti-symmetrized fragments and the corresponding density matrices to find deformation density matrix of each one. In the present study, two types of deformation density including kinetic energy pressure and relaxation analyses were accomplished for lithium and oxygen interaction at B3LYP/6-311+G\* theoretical level. Electronic deformation orbitals responsible for charge transfer were identified with respect to their eigenvalues. The results showed how these two competed with each other in neutral and charged complexes with different fragmentations.

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## 1 Introduction

Lithium-oxygen (Li-O<sub>2</sub>) batteries are a promising technology for energy storage due to their high theoretical energy density, low cost, and potential for use in electric vehicles and other applications [1–12]. However, the development of Li-O<sub>2</sub> batteries is hindered by several challenges, including the role of charge transfer in the battery [2]. Li-O<sub>2</sub> batteries are based on the same principles as traditional lithium-ion batteries, but instead of using a solid-state electrolyte, they use a porous carbon electrode and a liquid electrolyte [3–6]. The basic components of a Li-O<sub>2</sub> battery include a lithium metal anode, a porous carbon cathode, and a liquid electrolyte containing lithium salts [7, 8].

Charge transfer is a critical aspect of the operation of Li-O<sub>2</sub> batteries [1–5]. During discharge, lithium ions are oxidized at the anode and react with oxygen at the cathode to form lithium peroxide (Li<sub>2</sub>O<sub>2</sub>) [9–12]. This reaction involves the transfer of electrons from the anode to the cathode through an external circuit, generating electrical energy. During charge, the reverse reaction occurs, with lithium peroxide being oxidized at the cathode and lithium ions being reduced at the anode. This reaction also involves the transfer of electrons through an external circuit, which stores electrical energy in the battery. The efficiency of charge transfer in Li-O<sub>2</sub> batteries is critical for their performance. Poor charge transfer can lead to low energy efficiency, reduced cycle life, and safety issues, such as the formation of dendrites on the anode [3, 7, 8].

Although Li batteries possess many advantages, the development of Li-O<sub>2</sub> batteries is hindered by several challenges. One of the major challenges is the low energy efficiency of the battery. Li-O<sub>2</sub> batteries typically have an energy efficiency of less than 70%, which is lower than that of traditional lithium-ion batteries [1–5]. Another challenge is the formation of lithium peroxide on the cathode during discharge. The formation of lithium peroxide can lead to the clogging of the pores in the carbon electrode, which reduces the battery's performance and cycle life [3–5]. To overcome these challenges, several strategies have been proposed. One strategy is to use catalysts to promote the formation and decomposition of lithium peroxide on the cathode. Catalysts can improve the efficiency of charge transfer and reduce the formation of unwanted byproducts [1–6].

Electronic deformation density analysis has been transformed to a standard technique for identification and quantification of intermolecular interactions [13–18]. This method has been applied to different types of systems including steric interactions, block de-

formation, and conduction related phenomena [13–18]. For intermolecular interaction, it has been shown how the total deformation density can be decomposed into kinetic energy pressure and relaxation parts, which are abbreviated as TOT, KEP, and RLX throughout this research, and can be presented as electron deformation orbitals (EDOs) and their eigenvalues as qualitative and quantitative results [13–18]. The electron density reorganization due to an intermolecular interaction can be partitioned into two parts as kinetic KEP or Pauli repulsion interaction, and RLX interactions [16, 17], which are the repulsive steric and attractive interactions, respectively. Equations (1)–(3) displays deformation density formulations for total, KEP, and RLX, respectively:

$$\Delta\rho_{\text{TOT}} = \rho_{\text{complex}} - \rho_{\text{frags}}^0 \quad (1)$$

$$\Delta\rho_{\text{KEP}} = \rho_{\text{frags}}^{(A)} - \rho_{\text{frags}}^0 \quad (2)$$

$$\Delta\rho_{\text{RLX}} = \rho_{\text{complex}} - \rho_{\text{frags}}^{(A)} \quad (3)$$

where  $\rho_{\text{frags}}^{(A)}$ ,  $\rho_{\text{frags}}^0$ ,  $\rho_{\text{complex}}$  are responsible for charge densities of complex system, non-interacting fragments, and anti-symmetrized fragments with respect to fragments' molecular orbitals [16]. One of the important characteristics of deformation density is its symmetric eigenvalues with regards to their sign, i.e., each positive eigenvalue possesses corresponding eigenvalue with negative sign [16]. This property is necessary for the cases in which total number of electrons is conserved during the interaction. On the other hand, deformation density does not provide information per atom, i.e., individual atomic partitioning data is not available unless one considers atoms as fragments [17].

Oxidation and reduction are essential steps in Li-O<sub>2</sub> batteries. In molecular-scale, these two are associated to charge transfer between fragments and consequently can be assessed via charge reorganization. Hence, deformation density is a feasible technique for analysis of this type of interaction in lithium-oxygen interaction. Since chemical kinetics of oxygen reduction and evolution reactions in Li-O<sub>2</sub> batteries are relatively slow, sometimes they can be classified as low-energy efficient [8]. Therefore, the present study can help researchers in the field of lithium-oxygen interactions to get a deep look on how lithium and oxygen interact with each other via components of electronic deformation analysis.

## 2 Computational details

Molecular geometries and electronic wave functions are calculated at B3LYP/6–311+G\* utilizing Gaussian09 suite of programs [19]. Since conventional analysis of

chemical species requires the species to be thermodynamically stable, vibrational frequency calculations are also performed to identify minimum structures, i.e., to make sure no structure is classified as transition state. Reduction and oxidation are concepts which can be interpreted in the context of charge reorganization in an intermolecular interaction. Since deformation density analysis is able to trace charge displacement during that interaction, it can be employed to detect and quantify intermolecular charge transfer from each fragment to the other.

Interaction energies ( $E_{\text{int}}$ ) are calculated as the electronic energy difference between complex and fragments and deformation density analysis is also applied on neutral and charged complex to detect intermolecular interactions between lithium and oxygen and decompose into KEP, RLX parts that gives rise to TOT interactions via  $n_{\text{KEP}}$ ,  $n_{\text{RLX}}$ , and  $n_{\text{TOT}}$ , as sum of the corresponding eigenvalues, respectively. Densitizer program is also employed to detect intermolecular interactions in the context of deformation density anal-

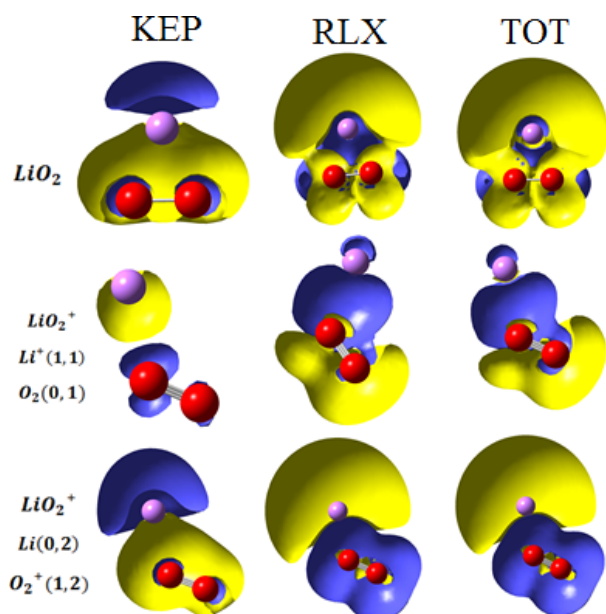
ysis and EDOs [20] and visualized using GaussView software [21].

### 3 Results and discussion

In this section, deformation density and interaction energy of three structures of  $\text{LiO}_2$  in neutral and cationic states have been investigated. In Table 1, the interaction energy and deformation density  $n_{\text{KEP}}$ ,  $n_{\text{RLX}}$  and  $n_{\text{TOT}}$  and their structures are reported in Figure 1. Yang et al. have used  $\text{Li}_2\text{O}_3$ ,  $\text{LiO}_4$ , and  $\text{LiO}_2$  crystal structures, which led to the formation of a lithium layer and improved the design and performance of lithium batteries [22]. Further, Lau et al. have investigated the thermodynamic stability of  $\text{LiO}_2$ ,  $\text{Li}_2\text{O}$  and  $\text{Li}_2\text{O}_2$  crystal structures [23]. Hong and Byon have considered singlet oxygen to find mechanism of oxygen production in  $\text{LiO}_2$  batteries [24] and, Soltay and Henderson have added  $\text{Li}_2\text{O}$  to silicate and germanate, which was different from other silicate glass containing alkaline oxides [25].

**Table 1.** Calculated relative interaction energy  $E_{\text{int}}$ , charge displacement due to steric effect ( $n_{\text{KEP}}$ ), relaxation ( $n_{\text{RLX}}$ ) and total interactions ( $n_{\text{TOT}}$ ) for  $\text{LiO}_2$  and  $\text{LiO}_2^+$  (All reported energies are in kcal/mol.)

Structure	Fragmentation	$n_{\text{KEP}}$	$n_{\text{RLX}}$	$n_{\text{TOT}}$	$E_{\text{int}}$
$\text{LiO}_2$	Li and $\text{O}_2$	0.58	2.46	2.54	-110.38
$\text{LiO}_2^+$	$\text{Li}^+$ and $\text{O}_2$	0.11	0.38	0.42	-10.47
$\text{LiO}_2^+$	Li and $\text{O}_2^+$	0.31	1.70	1.69	-678.10



**Fig. 1.** Deformation density isosurface (in yellow color for the depletion interactions (KEP) and in blue color for the concentration interactions (RLX)) for  $\text{LiO}_2$  and  $\text{LiO}_2^+$ .

We have also investigated molecular structure of both singlet and triplet oxygen for lithium-oxygen interaction in the present research. By examining the structure of  $\text{LiO}_2$  in the neutral state,  $n_{\text{RLX}}$  with a repulsion value of 2.46 is more than  $n_{\text{KEP}}$ , which indicates that the structure of  $\text{LiO}_2$  has more relaxation than repulsion. Furthermore, studying their structure in Figure 2 reveals that in KEP, the relaxation energy is more concentrated on lithium, and repulsion is concentrated on oxygen atoms, but in the RLX structure, the repulsion energy is on the whole structure, that the structure of  $\text{LiO}_2$  is affected by this repulsion and relaxation placed and the lithium atom is at the same distance from the oxygen atoms.

When  $\text{LiO}_2$  is in the cationic state, the  $n_{\text{KEP}}$ ,  $n_{\text{RLX}}$  and  $n_{\text{TOT}}$  energies are lower than in the neutral state  $\text{LiO}_2^+$  cation with the multiplicity of  $\text{Li}^+$  and  $\text{O}_2$  compared to the structure of  $\text{LiO}_2^+$  with the multiplicity of Li and  $\text{O}_2^+$  has the lower values of  $n_{\text{KEP}}$ ,  $n_{\text{RLX}}$  and  $n_{\text{TOT}}$  mean that repulsion energy and less relaxation are created in the structure. By more accurately investigating the  $\text{LiO}_2^+$  cation with the multiplicity of  $\text{Li}^+$  and  $\text{O}_2$  in this structure,  $n_{\text{RLX}}$  is more than  $n_{\text{KEP}}$  with

a value of 0.38. As shown in Figure 1, moreover, relaxation energy in the RLX structure, is more towards the lithium atom, but in the KEP structure, the repulsive energy is more on the lithium atom and the relaxation is on two oxygen atoms.

In the  $\text{LiO}_2^+$  cation with the multiplicity of Li and  $\text{O}_2^+$ ,  $n_{\text{RLX}}$  with a value of 1.7 is more than  $n_{\text{KEP}}$ , and according to Figure 1, in the structure of KEP, relaxation energy is located on the lithium atom and repulsion on the oxygen atoms, but in the RLX structure, relaxation and repulsion energy covers the oxygen atom and surrounds them.

According to the investigations on the two cationic states of  $\text{LiO}_2^+$ , it can be stated that the repulsive and relaxation energy in the two structures of KEP and RLX are inverted; that is, in the KEP structure,  $\text{LiO}_2^+$  with the multiplicity of  $\text{Li}^+$  and  $\text{O}_2$ , the relaxation energy is on the lithium atom, but in the  $\text{LiO}_2^+$  structure with the multiplicity of  $\text{Li}(2)$  and  $\text{O}_2^+$ , the relaxation energy is placed on two oxygen atoms. In the structure of RLX  $\text{LiO}_2^+$ , with the multiplicity of  $\text{Li}^+$  and  $\text{O}_2$ , the repulsive energy on the lithium atom, but in  $\text{LiO}_2^+$ , with the multiplicity of Li and  $\text{O}_2^+$ , the repulsive energy is on two oxygen atoms.

The interaction energy in the cation state of  $\text{LiO}_2^+$  with the multiplicity of Li and  $\text{O}_2^+$  with a negative value of  $-10.47$  is higher than the other two neutral and cationic structures because it has a lower deformation density than the other two structures. In general, KEP and RLX work toward opposite directions as repulsive and attractive interactions. While RLX tends to bring molecular orbitals of the fragments together to establish stronger interaction, KEP avoids molecular orbitals of fragments to get closed. Therefore, one may include other chemical species or substrate to minimize the KEP interaction, while maximizing the RLX interaction as much as possible results into higher efficiency of the involved chemical reactions. Liu et al. used density functional theory simulation and have shown that synergy can improve the performance of  $\text{LiO}_2$  batteries on the graphene oxide surface [26]. Since the mechanism of the reaction of lithium-oxygen cells in cathode processes is very difficult, Liu et al. applied theoretical techniques to improve  $\text{LiO}_2$  battery power density and the extra energy needed for  $\text{LiO}_2$  electrolysis [27].

In order to get orbital picture of lithium oxygen interaction, EDOs and their eigenvalues are plotted in Figures 2 and 3 for  $\text{LiO}_2$  and  $\text{LiO}_2^+$ , respectively. According to Figure 2, the most significant positive EDO of KEP correspond to 0.42 electron which possesses a nodal behavior at the middle of lithium oxygen area, while the EDO with  $-0.44$  electron is a uniform orbital located on the whole complex. The eigenvalues of RLX are much larger than KEP and confirm RLX as

dominant interaction. Dominance of RLX over KEP is also reflected in the TOT, as their shape and nodal structure are quite similar.

By simulating density functional theory, Liu et al. showed that synergy can improve the performance of  $\text{Li-O}_2$  batteries on the graphene surface of the oxide.

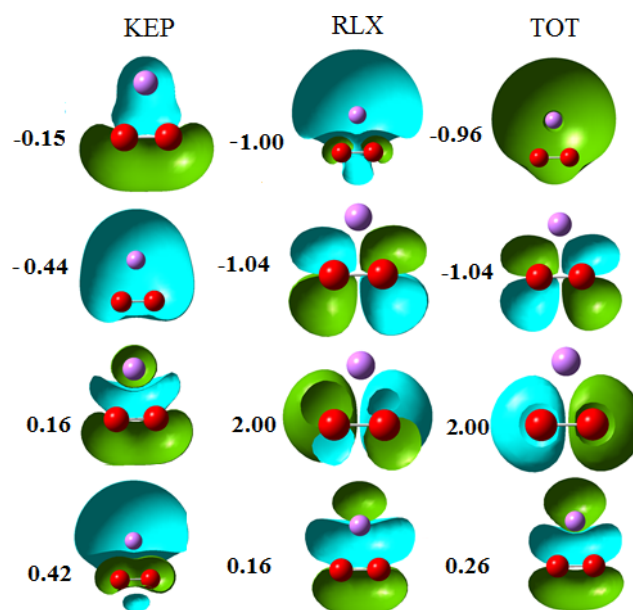


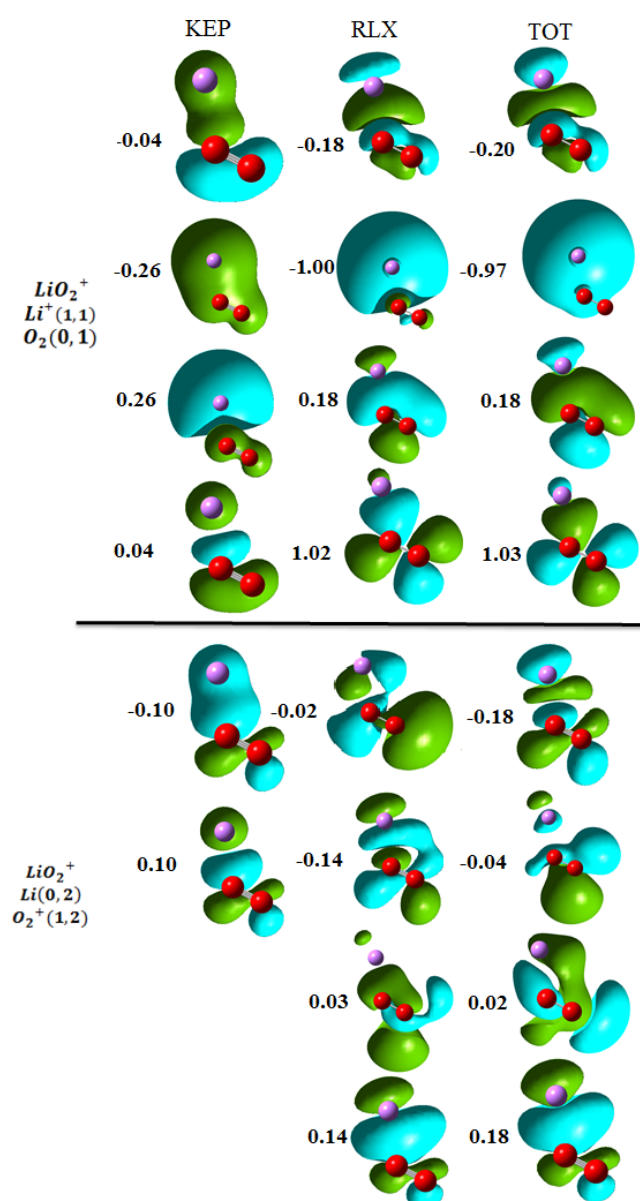
Fig. 2. EDOs and their eigenvalues for interaction between neutral lithium and oxygen molecule.

The intermolecular interactions in charged lithium-oxygen complex are shown in Figure 3, where the two possible fragmentations are separated by a horizontal line. While  $\text{LiO}_2$  structure is symmetric in Figure 2, its cation possesses  $C_s$  point group in Figure 3. The distribution of eigenvalues and shapes of EDOs are also different from neutral  $\text{LiO}_2$  in Figure 2. However, similar to Figure 2, Figure 3 also shows dominance of RLX over KEP for both fragmentations. The eigenvalues of RLX and TOT are similar and shape of EDOs has negligible differences. In the first fragmentation in the top of Figure 3, there exist two eigenvalues as large as 1.00, showing strong charge transfer from lithium cation to oxygen molecule. Such large eigenvalue does not exist for the bottom fragmentation in which lithium is in its neutral state. Xia et al. also analyzed electron transfer process in oxygen atoms in lithium and oxygen-based batteries, which resulted in a decrease in two oxygen electrons and  $\text{Li}_2\text{O}_2$  formation [28].

## 4 Conclusion

The interaction between lithium and oxygen is a complex process that can be studied in the context of electronic deformation density analysis. The formation of

unwanted reaction products and the stability of the lithium electrode are major challenges that need to be addressed to realize the full potential of lithium-oxygen batteries and several strategies can be used to analyze the corresponding physical and chemical interactions. In the present study, the lithium oxygen interaction is decomposed into two kinetic energy pressure and relaxation parts, where two types of fragmentations are used for lithium and oxygen. The findings revealed that both components are present in the lithium oxygen interaction and charge is transferred from both fragments.



**Fig. 3.** EDOs and their eigenvalues for  $\text{LiO}_2^+$ , where two types of fragmentations are considered.

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