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Charge distribution and lithium-oxide stability modeled by reactive force field

Vjeran Gomzi, Jakov Juvančić
Faculty of electrical engineering and computing, University of Zagreb, Unska 3, Zagreb, Croatia

srce | Sveučilište u Zagrebu Sveučilišni računski centar

Vjeran.Gomzi@fer.unizg.hr

INTRODUCTION

Understanding of lithium and its oxidation processes is of interest in design and development of lithium-based batteries, especially these based on lithium-air technology. Despite their advantages (energy density similar to gasoline) over conventional Li-ion batteries, its efficiency is still lower, so the catalytic approach is used for possible improvements.

Investigation of a large reaction space is often much more efficient using *in-silico* methods. Molecular dynamics using the Reactive force field approach as applied in the *ReaxFF* package is promising method optimizing simulation capabilities and calculation efficiency [1].

The charge distribution and especially electron transfer reactions are expected to be better described in *ReaxFF* using the novel atom-condensed Kohn-Sham DFT (ACKS2) charge interaction method, than the electronegativity equalisation method (EEM) used previously [2]. However, the use of the novel method requires re-optimization of the whole force field.

In *Part I* we investigate the effect of the use of the charge interaction model on theoretical prediction of charge distribution in lithium oxides and compare these with *ab initio* results. In *Part II* we attempt to develop the ACKS2-based force field capable of reasonable reproduction of experimentally observed crystals in all lithium oxides (i.e. LiO, Li_2O, LiO_2, Li_2O_2, LiO_3).

Methods I

Python3 routine for calculation of interaction energy and charge distribution using the reactive force field either by application of EEM or ACKS2 charge interaction model is prepared in course of one of the authors bachelor's work (JJ). The program used simplified energy calculation neglecting bond-order and other interatomic interactions and is used mainly for calculation of charge distribution:

$$E_{system} = E_{bond} + E_{overcoordination} + E_{angle} + E_{torsion} + E_{vdWaals} + E_{charge}$$

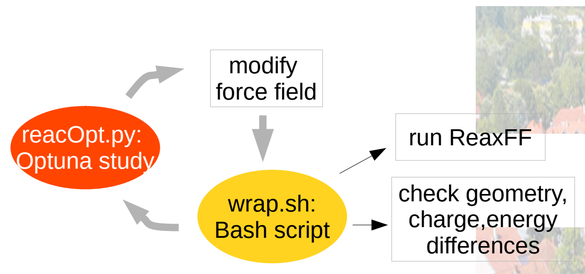
The charge distribution is also calculated applying density-functional theory calculations using *Gaussian 16* with B3PW91/LanlDZ2 density functional/basis set and *abinit* using ultrasoft periodic potential packages run on *Supek* HPC cluster at SRCE for validation of results.

The developed code is applied on all the lithium oxides Li_2O, LiO_2, Li_2O_2 and LiO_3 at their crystal structure and as isolated molecules using available force fields [3]. As much of the energy contributions were missing in the test python code, the comparison was primarily targeted at restricted geometries in their crystal positions.

Methods II

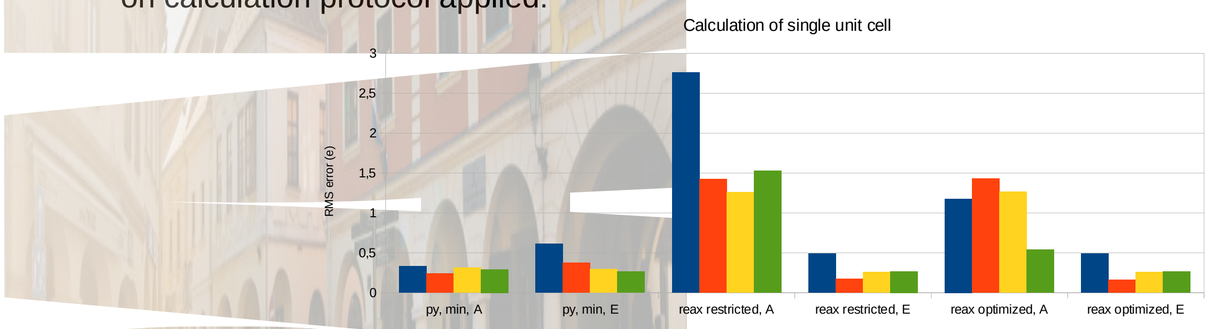
The *ReaxFF* code uses parabolic optimization of independent parameters. Alternative approach is designed using *Optuna* code and additional software for structure comparison. These modules are wrapped in *Python3* and *bash shell* script for handling multiple calculations in *ReaxFF* code. Such an optimization process is applied using the crystal and optimized structures of all the lithia oxides mentioned in Part I as training set.

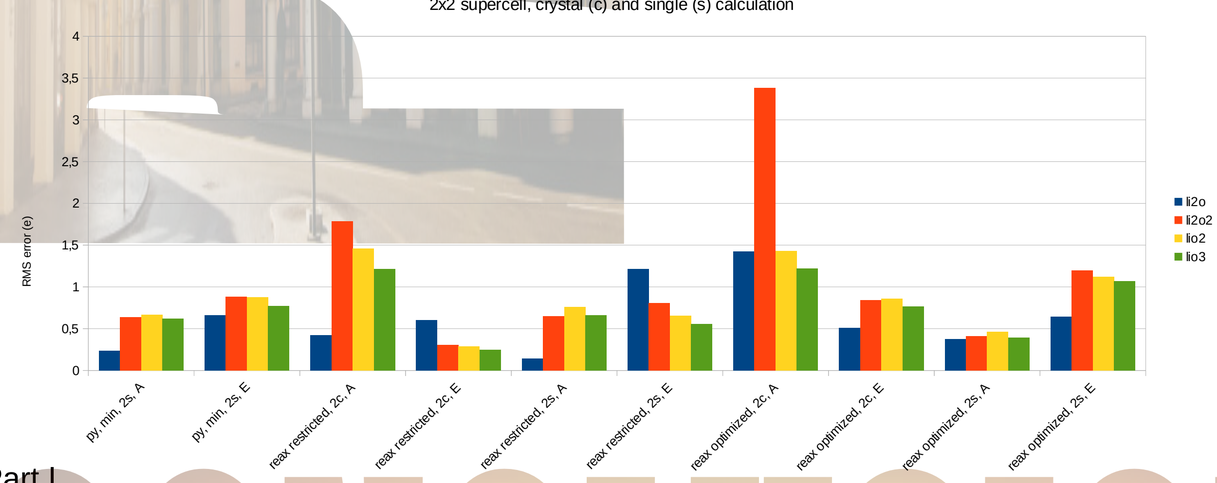
Parameter optimization is performed also on the 'old' EEM force field for comparison [3]. The parameters are validated by capability of the optimized force field to describe stable structures of pure lithium crystal as well as the LiO_2 crystal.



Results I

All charges predicted by the use of reactive force-field method, using both the EEM and ACKS2 approach are compared with respective theoretical calculations. Squares of differences of predicted charges at respective atoms in all the investigated structures are summed and root-mean square error is calculated. The obtained data is presented in charts below showing dependence of RMS of charge on calculation protocol applied:





Results II

Parabolic optimization process is both laborious and lengthy, although relatively safe method for optimization of a considerable number of optimization parameters (as much as 40 here). It however fails if parameters may be related. The parameters were optimized using this method successfully only upon reversing the order of parameters to optimize (representing probably the level of parameter importance and effects on other subsequent parameters trying to optimize from the least important to the most important ones.)

Performance of several optimization protocols is summarized in Table below.

				Li crystal (864 atoms)		LiO_2 crystal (1500 atoms)	
Optimization type	Force field	Num. params.	Optimization duration	Largest cluster	Total number of fragments	Largest cluster	Total number of fragments
parabolic	ACKS2	40	~ 30 days	Li2	432	O887Li470	93
python/Optuna + wrapper	ACKS2	40	~ 2 days	Li864	1	O247Li497	379
python/Optuna + wrapper	ACKS2	49	~ 3 days	Li863	2	Li472	390
python/Optuna + wrapper	EEM	39	~ 2 days	Li864	1	O275Li486	366
reference field [3a]	EEM	-	-	Li864	1	O536Li495	234
reference field [3b]	ACKS2	-	-	Li4	431	O606Li336	224

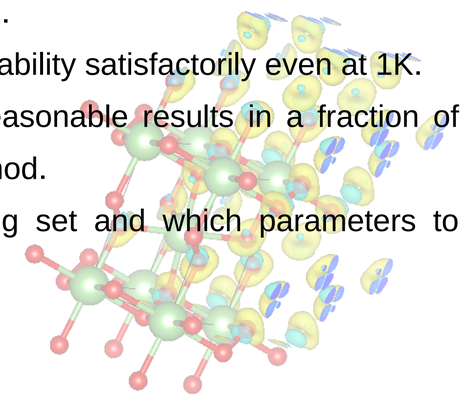
CONCLUSIONS

Part I

- Results are quite unexpected: the ACKS2 approach reproduces DFT atomic charges with quality depending on the structure investigated, as well as on the geometry optimization of the structure. It is also somewhat more computationally demanding (up to 3 times longer calculation times).
- This implementation is thus not satisfactory, as we are interested in the force field able to model reactions and oxidation state changes.

Part II

- [Rows 2&4] Developed force fields (both EEM and ACKS2 type) that reproduce stable crystal structures (Li and Li_2O, for example).
- [Columns 7&8] Not managed to reproduce LiO_2 stability satisfactorily even at 1K.
- [Column 3] Novel optimization protocol yields reasonable results in a fraction of time in comparison to the standard parabolic method.
- [Rows 2&3] Important to choose correct training set and which parameters to optimize!



References

[1] T. P. Senftle *et. al.* (2016) *npj Comput. Mat.* 2: 15011.
[2] T. Verstraelen, P. W. Ayers, V. Van Speybroeck, M. Waroquier (2013) *J. Chem. Phys.* 138, 074108.
[3] (a) A. Ostadhossein, S.-Y. Kim, E. D. Cubuk, Y. Qi, A. C. T. van Duin (2016) *J. Phys. Chem. A*, 120 (13), pp 2114-2127; (b) K. A. O'Hearn *et al.* (2020) *J. Chem. Phys.* 153, 084107.