

popoff: POtential Parameter Optimisation for Force-Fields

Lucy M. Morgan^{1, 2}, Matt J. Clarke¹, M. Saiful Islam^{1, 2}, and Benjamin J. Morgan^{1, 2}

¹ Department of Chemistry, University of Bath, Claverton Down, UK, BA2 7AY ² The Faraday Institution, Quad One, Harwell Campus, Didcot, OX11 0RA, UK

DOI: [10.21105/joss.03747](https://doi.org/10.21105/joss.03747)

Software

- [Review](#) ↗
- [Repository](#) ↗
- [Archive](#) ↗

Editor: [David P. Sanders](#) ↗

Reviewers:

- [@marshallmcdonnell](#)
- [@lscalfi](#)

Submitted: 02 July 2021

Published: 21 September 2021

License

Authors of papers retain copyright and release the work under a Creative Commons Attribution 4.0 International License ([CC BY 4.0](#)).

Statement of need

Interatomic potentials give an approximate mathematical description of the interactions between atoms in a given system. These interactions are unique to the species and the surrounding environment, yet in the wider literature interatomic potentials between specific atom types, for example Li-O, are reused in vastly different systems. This is particularly familiar for the O-O potential derived by Jackson and Catlow in 1985 for UO_2 , ([Jackson & Catlow, 1985](#)) which has since been used in the study of many materials, in particular ionic solids. Although in some cases the species interactions may not vary substantially between different materials, in other cases it does, and to varying degrees. For example, a particular metal-oxygen interaction in a spinel might be considerably different to that in a layered oxide material, due in part to the charge distribution increasing the influence of polarizability. It is therefore crucial to develop interatomic potentials for individual systems to get the best approximation of the interactions within that environment.

There are a limited number of codes available with the explicit purpose or functionality for fitting potentials. Most of which require some pre-requisite knowledge of coding or specialism, creating a prohibitive barrier for utilising these tools in the wider atomistic modelling research community. These codes are also not able to account for all aspects which may need to be considered for particular materials, such as polarizability. Creating a resource, with minimal pre-requisite requirements to use, and able to account for a larger range of material considerations needed for accurate potentials is therefore key to producing more robust classical MD investigations.

Summary

PopOff is a Python package for fitting Coulomb-Buckingham type interatomic potentials for classical potential-based molecular dynamics (MD). This is a modular fitting code, allowing increased control over several important aspects of the potential. Formal charge, partial charge, or a charge scaling factor can be fitted. A rigid ion model, a core-shell model, or mixture of both can be chosen. If choosing to fit a core-shell model, the charge separation over the core and shell components can be fixed or fitted, as can the spring constant. Individual Buckingham parameters can also be selectively fixed, fitted, or set to zero. PopOff currently fits to first principles derived forces and stress tensors obtained from a VASP (The Vienna Ab initio Simulation Package: atomic scale materials modelling from first principles) ([Kresse & Furthmüller, 1996a, 1996b](#); [Kresse & Hafner, 1993, 1994](#)) training set through the `vasprun.xml` output files. LAMMPS (Large-scale Atomic/Molecular Massively Parallel Simulator), ([Plimpton, 1995](#)) a classical MD code with a focus on materials modeling, is used as a

backend to perform the MD during the fitting process and outputs the forces and stress tensors, produced using a range of potentials from the search space. The output atom forces and system stress tensors are compared and minimised.

The development of sufficiently accurate interatomic potentials, which requires model parameterization with respect to a set of target observables, for a specific chemistry is quite challenging, especially for complex systems. For example, in layered structures, such as the widely used LiNiO₂ based cathode materials, the short-range interactions are overwhelmed by the longer-range Coulombic term. In these cases, the system charges need to be scaled down to increase the influence of the short-range interactions, termed as partial charges, and the influence of polarizability needs to be included, usually through using a core-shell model. Variations of the Buckingham potential have been developed for these systems, some using rigid ion models, (Dawson & Tanaka, 2014; Ledwaba et al., 2020; Lewis & Catlow, 1985; Sayle et al., 2005) and others using core-shell models, (Ammundsen et al., 1999; Fisher et al., 2010; Hart & Bates, 1998; He et al., 2019; Kerisit et al., 2014; Lee & Park, 2012; Lewis & Catlow, 1985) with a mixture of formal and partial charges being used. Interatomic potentials are traditionally based on mathematical functions which have been parameterized using experimental and/or First Principles derived data (Buckingham, 1938; Jones, 1924). There are a limited number of codes available with the explicit purpose or functionality for fitting potentials. Fitting routines from established codes including the General Utility Lattice Program (GULP), (Gale, 1997) Atomicrex, (Stukowski et al., 2017) dftfit, (Ostrouchov, n.d.) and potfit (Wen et al., 2017) each possess unique functionality, however, none are fully able to produce robust potentials for NMC or LiNiO₂ due to different aspects not being considered within the code, such as charge scaling or core-shell models. PopOff has been specifically developed for fitting different permutations of the Buckingham potential. Its modular design allows flexible fitting of both rigid ion and core-shell models, and formal and partial charges.

We are currently using PopOff in our own research to develop potentials for cathode and solid-electrolyte materials for classical MD analysis of Li⁺/Na⁺ migration properties. PopOff is also being used by a group at Newcastle University to develop potentials for several halide based solid-electrolyte materials in collaboration with experimental partners. We hope that this open-source resource will support development of interatomic potentials tailored to individual systems, and thus results in better approximations of the atomic interactions.

Optimiser

PopOff uses `scipy.optimize.differential_evolution` as its global optimiser to optimise the function that calculates the mean squared error between the forces and stress tensors within the training set and those calculated with possible classical MD potentials, via:

$$\chi^2 = \frac{1}{n} \sum_{i=1}^n (Y_i - \hat{Y}_i)^2$$

where n is the number of data points, Y_i is the observed values, and \hat{Y}_i is the predicted values.

Differential evolution is a stochastic population-based method, where at each pass through the population the algorithm mutates each candidate solution by mixing with other candidate solutions to create a trial candidate. There are several strategy methods which can be used to create the trial candidate, with `latinhypercube` used as default.

PopOff's modular design allows the code to fit the following parameters:

- A rigid ion model, a core-shell model, or mixture of both.

- 83 ▪ For a core-shell model, the charge separation over the core and shell components can
- 84 be fixed or fitted as can the spring constant.
- 85 ▪ Selectively fix, fit, or set to zero the individual Buckingham parameters.

86 Approximations and Limitations

- 87 ▪ Due to the different orders of magnitude between the forces acting on the atoms and
- 88 the stress tensors of the system, the stress tensors are scaled by *0.001 to give higher
- 89 weighting to the forces. This can be changed in `fitting_code.py`, however, this is
- 90 not given as a suggested change in the manual.
- 91 ▪ Care needs to be taken in choosing the cutoff value, which must be less than half
- 92 minimum cell width to prevent self interactions. This value is set as 10 Angstroms as
- 93 default and can be changed in the `fitting_code.py`, however, this is not given as a
- 94 suggested change in the manual.

95 Acknowledgements

96 L. M. M. acknowledges support from the Faraday Institution (faraday.ac.uk; EP/S003053/1:
97 Grant No. FIRG003). Additional support was received from the Royal Society (UF130329,
98 URF\R\191006).

99 References

- 100 Ammundsen, B., Burns, G. R., Islam, M. S., Kanoh, H., & Rozière, J. (1999). Lattice
101 Dynamics and Vibrational Spectra of Lithium Manganese Oxides: A Computer Simulation
102 and Spectroscopic Study. *The Journal of Physical Chemistry B*, 103(25), 5175–5180.
103 <https://doi.org/10.1021/jp984398l>
- 104 Buckingham, R. A. (1938). The classical equation of state of gaseous helium, neon and
105 argon. *Proceedings of the Royal Society of London. Series A. Mathematical and Physical*
106 *Sciences*, 168(933), 264–283. <https://doi.org/10.1098/rspa.1938.0173>
- 107 Dawson, J. A., & Tanaka, I. (2014). Oxygen Vacancy Formation and Reduction Proper-
108 ties of β -MnO₂ Grain Boundaries and the Potential for High Electrochemical Perfor-
109 mance. *ACS Applied Materials & Interfaces*, 6(20), 17776–17784. [https://doi.org/10.](https://doi.org/10.1021/am504351p)
110 [1021/am504351p](https://doi.org/10.1021/am504351p)
- 111 Fisher, C. A. J., Islam, M. S., & Moriwake, H. (2010). Atomic Level Investigations of Lithium
112 Ion Battery Cathode Materials. *Journal of the Physical Society of Japan*, 79(Suppl.A),
113 59–64. <https://doi.org/10.1143/JPSJS.79SA.59>
- 114 Gale, J. D. (1997). GULP: A computer program for the symmetry-adapted simulation of
115 solids. *Journal of the Chemical Society, Faraday Transactions*, 93(4), 629–637. [https:](https://doi.org/10.1039/a606455h)
116 [//doi.org/10.1039/a606455h](https://doi.org/10.1039/a606455h)
- 117 Hart, F. X., & Bates, J. B. (1998). Lattice model calculation of the strain energy density and
118 other properties of crystalline LiCoO₂. *Journal of Applied Physics*, 83(12), 7560–7566.
119 <https://doi.org/10.1063/1.367521>
- 120 He, J., Zhang, L., & Liu, L. (2019). Thermal transport in monocrystalline and polycrystalline
121 lithium cobalt oxide. *Physical Chemistry Chemical Physics*, 21, 12192–12200. [https:](https://doi.org/10.1039/C9CP01585J)
122 [//doi.org/10.1039/C9CP01585J](https://doi.org/10.1039/C9CP01585J)

- 123 Jackson, R. A., & Catlow, C. R. A. (1985). Trapping and solution of fission Xe in UO_2 .:
124 Part 1. Single gas atoms and solution from underpressurized bubbles. *Journal of Nuclear*
125 *Materials*, 127(2-3), 161–166.
- 126 Jones, J. E. (1924). On the determination of molecular fields. -II. From the equation of state
127 of a gas. *Proceedings of the Royal Society of London. Series A, Containing Papers of a*
128 *Mathematical and Physical Character*, 106(738), 463–477. <https://doi.org/10.1098/rspa.1924.0082>
129
- 130 Kerisit, S., Chaka, A. M., Droubay, T. C., & Ilton, E. S. (2014). Shell Model for Atom-
131 istic Simulation of Lithium Diffusion in Mixed Mn/Ti Oxides. *The Journal of Physical*
132 *Chemistry C*, 118(42), 24231–24239. <https://doi.org/10.1021/jp506025k>
- 133 Kresse, G., & Furthmüller, J. (1996a). Efficiency of ab-initio total energy calculations for
134 metals and semiconductors using a plane-wave basis set. *Computational Materials Science*,
135 6(1), 15–50.
- 136 Kresse, G., & Furthmüller, J. (1996b). Efficient iterative schemes for ab initio total-energy
137 calculations using a plane-wave basis set. *Physical Review B*, 54(16), 11169.
- 138 Kresse, G., & Hafner, J. (1993). Ab initio molecular dynamics for liquid metals. *Physical*
139 *Review B*, 47(1), 558.
- 140 Kresse, G., & Hafner, J. (1994). Ab initio molecular-dynamics simulation of the liquid-metal-
141 amorphous-semiconductor transition in germanium. *Physical Review B*, 49(20), 14251.
- 142 Ledwaba, R. S., Sayle, D. C., & Ngoepe, P. E. (2020). Atomistic Simulation and Characteri-
143 zation of Spinel $\text{Li}_{1+x}\text{Mn}_2\text{O}_4$ ($0 \leq x \leq 1$) Nanoparticles. *ACS Applied Energy Materials*,
144 3(2), 1429–1438. <https://doi.org/10.1021/acsaem.9b01870>
- 145 Lee, S., & Park, S. S. (2012). Atomistic simulation study of mixed-metal oxide
146 ($\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$) cathode material for lithium ion battery. *The Journal of*
147 *Physical Chemistry C*, 116(10), 6484–6489.
- 148 Lewis, G. V., & Catlow, C. R. A. (1985). Potential models for ionic oxides. *Journal of Physics*
149 *C: Solid State Physics*, 18(6), 1149–1161. <https://doi.org/10.1088/0022-3719/18/6/010>
- 150 Ostrouchov, C. (n.d.). *dftfit*. Retrieved September 29, 2020, from <https://chrisostrouchov.com/dftfit>
151
- 152 Plimpton, S. (1995). Fast parallel algorithms for short-range molecular dynamics. *Journal of*
153 *Computational Physics*, 117(1), 1–19.
- 154 Sayle, T. X. T., Catlow, C. R. A., Maphanga, R. R., Ngoepe, P. E., & Sayle, D. C. (2005).
155 Generating MnO_2 Nanoparticles Using Simulated Amorphization and Recrystallization.
156 *Journal of the American Chemical Society*, 127(37), 12828–12837. <https://doi.org/10.1021/ja0434073>
157
- 158 Stukowski, A., Fransson, E., Mock, M., & Erhart, P. (2017). Atomicrex—a general purpose tool
159 for the construction of atomic interaction models. *Modelling and Simulation in Materials*
160 *Science and Engineering*, 25(5), 055003. <https://doi.org/10.1088/1361-651x/aa6ecf>
- 161 Wen, M., Li, J., Brommer, P., Elliott, R. S., Sethna, J. P., & Tadmor, E. B. (2017). A
162 KIM-compliant *potfit* for fitting sloppy interatomic potentials: application to the EDIP
163 model for silicon. *Modelling and Simulation in Materials Science and Engineering*, 25(1),
164 014001. <https://doi.org/10.1088/0965-0393/25/1/014001>