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MacroDensity: Analysis of electrostatic potential and electron density landscapes of crystals

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Summary

We report a Python package to simplify the analysis of electrostatic potentials and electron density of crystals. Macrodensity can read volumetric output files from the first-principles materials modelling codes VASP (LOCPOT format) and FHI-AIMS (cube format), as well as the classical electrostatic potentials from GULP (standard output). The code consists of functions that calculate and plot planar macroscopic and spherical averages, as well as calculating conduction and valence band alignments over a user-defined vector or plane. As a result, this code has been used to aid the data analysis and generation for several publications(Butler et al., 2014, p. @Walsh:2013).

Statement of need

To assess the potential utility of novel semiconducting devices (like p-n junctions, heterostructures, surface terminations), it is key to understand how the electrostatic potential and electron density change across the system (Politzer & Murray, 2002). However, analysing this data from the raw output of simulations can prove cumbersome and often requires manually extracting data and using visualisation software. This can result in bottlenecks in high throughput screening projects, where the same data extraction procedure is repeatedly applied to large databases of candidate structures.

The general approach for processing electrostatic potential and electron density data as well as its translation to a grid mesh is discussed in Butler et al. (2014). Withing the framework of Kohn-Sham density functional theory, this approach samples the spherical averages over points within the system onto a matrix, where our raw data is generated. To process this data appropriately, `MacroDensity` was developed to simplify the data extraction and visualisation processes. By defining planes or vectors along the landscape of electrostatic potentials and electronic density matrix, it becomes straightforward to produce meaningful analysis and visualisation plots across a user-defined area.

MacroDensity

`MacroDensity` is a set of Python modules developed to read and analyse electrostatic potentials and electron density data from electronic structure calculations derived from Density Functional Theory (DFT) (Kohn et al., 1996). The package allows users to read from VASP (Kresse & Furthmüller, 1996) LOCPOT and CHGCAR files, FHI-AIMS (Blum et al., 2009) (cube file), and GULP (Gale, 1997) (standard output files) and format the data into physically meaningful quantities, which can then be plotted for user interpretation.

The package formats datasets containing information about a system's lattice parameters, electron density, and electrostatic potentials. `MacroDensity` contains some high-level tools and functions to calculate and plot the planar and macroscopic average as defined in Jackson's Electrodynamics (Jackson, 2003) (Figure 1a). The determination of the lattice vector settings and how the macroscopic averaging is calculated in this package is best described from the work of Peressi et al. (1998).

$$\overline{f}(z) = \frac{1}{S}\int_S f(x,y,z)\,dxdy \tag{1}$$

`MacroDensity` can also calculate and plot the localised potential around a certain atomic nucleus of a system. The approach to calculating this on-site (Hartree) potential is similar to calculating the Madelung potential (Figure 1b). This is useful for electron energy level predictions (Walsh & Butler, 2013). In addition, the spherical average around a user-defined point within the system can be calculated using an approach akin to the planar average function (integrating over a sphere instead of a plane). Similarly, instead of averaging over a sphere, `MacroDensity` can also calculate the average and macroscopic potentials within a specified volume of a cube which moves along a plane of the system's lattice.

Calculations and averaging at different points in space can be used to quantify the valence band and conduction band positions relative to this average. This is a convenience function that is included within the package, which calculates the bulk interstitial alignment similarly to that from Frensley & Kroemer (1976).

$$V_M = \sum_{i,j}\frac{(-1)^{n_i+n_j}}{4\pi\varepsilon_0 r_{ij}} \tag{2}$$

`MacroDensity` has been used to rapidly generate data for the publications Butler et al. (2014) and Walsh & Butler (2013) amongst others.

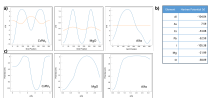

Figure 1: Example analysis done with the package for AlAs, CsPbI3, and MgO: a) plots of the planar (blue) and macroscopic (orange) averages of the potential, b) plots of the mean potential along the [111] vector, c) onsite (Hartree) potentials of the constituent atoms of the compounds analysed.

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Blum, V., Gehrke, R., Hanke, F., Havu, P., Havu, V., Ren, X., Reuter, K., & Scheffler, M. (2009). Ab initio molecular simulations with numeric atom-centered orbitals. *Computer Physics Communications*, *180*(11), 2175–2196. https://doi.org/10.1016/j.cpc.2009.06.022

Butler, K. T., Hendon, C. H., & Walsh, A. (2014). Electronic chemical potentials of porous metalOrganic frameworks. *Journal of the American Chemical Society*, *136*(7), 2703–2706. https://doi.org/10.1021/ja4110073

Frensley, W. R., & Kroemer, H. (1976). Prediction of semiconductor heterojunction discontinuities from bulk band structures. *Journal of Vacuum Science and Technology*, *13*(4), 810–815. https://doi.org/10.1116/1.568995

Gale, J. D. (1997). GULP: A computer program for the symmetry-adapted simulation of solids. *Journal of the Chemical Society, Faraday Transactions*, *93*(4), 629–637. https://doi.org/10.1039/a606455h

Jackson, J. D. (2003). *Electrodynamics, classical*. Wiley-VCH Verlag GmbH & Co. KGaA. https://doi.org/10.1002/3527600434.eap109

Kohn, W., Becke, A. D., & Parr, R. G. (1996). Density functional theory of electronic structure. *The Journal of Physical Chemistry*, *100*(31), 12974–12980. https://doi.org/10.1021/jp9606691

Kresse, G., & Furthmüller, J. (1996). Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. *Physical Review B*, *54*(16), 11169. https://doi.org/10.1103/PhysRevB.54.11169

Peressi, M., Binggeli, N., & Baldereschi, A. (1998). Band engineering at interfaces: Theory and numerical experiments. *Journal of Physics D: Applied Physics*, *31*(11), 1273–1299. https://doi.org/10.1088/0022-3727/31/11/002

Politzer, P., & Murray, J. S. (2002). The fundamental nature and role of the electrostatic potential in atoms and molecules. *Theoretical Chemistry Accounts: Theory, Computation, and Modeling (Theoretica Chimica Acta)*, *108*(3), 134–142. https://doi.org/10.1007/s00214-002-0363-9

Walsh, A., & Butler, K. T. (2013). Prediction of electron energies in metal oxides. *Accounts of Chemical Research*, *47*(2), 364–372. https://doi.org/10.1021/ar400115x