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Effect of Long-Range Dispersion DFT Functionals in Modelling Li-ion Transport in Layered MXenes

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Abstract

The abstract goes here.

Introduction

High-performance electrochemical storage devices are gaining attention due to the promise of meeting the increasing demand for energy storage for renewable energy sources as well as for electric vehicles. The gravimetric and volumetric energy densities of existing battery technologies are, however, not comparable to that of gasoline, and consequently electric vehicles are not currently a competitive alternative to fossil fuelled cars.¹ **[FiXme Note: batteries as focus?]**

FiXme

An emerging class of 2D early transition metal materials, the so-called MXenes ($M_{n+1}X_nT_x$ for $n = 1, 2, 3$, where M is an early transition metal (e.g. Sc, Ti, V, Hf etc.), X = C, N and T is a functional termination group (typically either O, OH or F), have been of interest within many fields, including Li-ion batteries. MXenes, are hexagonal layered materials, which are bound by the long range effects, making the description of these dispersion effects of paramount importance when describing properties of stacked MXenes.²⁻⁴ **[FiXme Note:**

Note!

FiXme

I really don't like this phrasing.] The monolayer can be seen in Fig. 1

Note!

Figure 1: (a) Top view of MXene. (b) Side view.

In Density Functional Theory (DFT), these effects must be accounted for explicitly in the functional, or as a correction, which has been done in several works⁵⁻⁸ - however, the

magnitude of the vdW correction is not unique, and must therefore be tested in the particular system in question. In this work, a selection of long range dispersion functionals will be benchmarked for MXenes, in particular Ti_2C , in order to determine the most appropriate functional. **[FiXme Note: Define "appropriate" functional]**

FiXme
Note!

Computational Methods

The DFT calculations in this work were performed in the Vienna Ab initio Simulation Package (VASP)⁹ along with the Atomic Simulation Environment (ASE)¹⁰. The projector augmented wave (PAW)¹¹ method, combined with pseudopotentials¹², was used to describe the core electrons. The valence electrons were described by a plane-wave basis set with a 950 eV energy cutoff **[FiXme Note: comment on the fairly high cutoff energy?]**. The exchange-correlation (xc) functionals which have been investigated in this work include: the Perdew-Burke-Ernzerhof (PBE)¹³ form of the generalized gradient approximation (GGA) coupled with the D3⁵ method for the long range dispersion corrections; the opt-B88-vdW⁷ functional; and finally the vdW-DF2⁶ functional. **[FiXme Note: Add which pseudopotentials? How?]**

FiXme
Note!

FiXme
Note!

A smearing of 0.05 eV was applied for the occupation of electronic states, and the calculations were spin-unpolarized. The Brillouin zone was sampled using a Γ -centered Monkhorst-Pack k -point mesh¹⁴ - a $9 \times 9 \times 1$ sampling was used to describe the unit cell in of a monolayer and $9 \times 9 \times 9$ for the unit cell of the bulk. **[FiXme Note: I guess we should also touch on the size of the k-point mesh in the supercells?]**

FiXme
Note!

Results and Discussion

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