



# Cyclic density functional theory: A route to the first principles simulation of bending in nanostructures



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## ABSTRACT

We formulate and implement Cyclic Density Functional Theory (Cyclic DFT) – a self-consistent first principles simulation method for nanostructures with cyclic symmetries. Using arguments based on Group Representation Theory, we rigorously demonstrate that the Kohn-Sham eigenvalue problem for such systems can be reduced to a fundamental domain (or cyclic unit cell) augmented with cyclic-Bloch boundary conditions. Analogously, the equations of electrostatics appearing in Kohn-Sham theory can be reduced to the fundamental domain augmented with cyclic boundary conditions. By making use of this symmetry cell reduction, we show that the electronic ground-state energy and the Hellmann-Feynman forces on the atoms can be calculated using quantities defined over the fundamental domain. We develop a symmetry-adapted finite-difference discretization scheme to obtain a fully functional numerical realization of the proposed approach. We verify that our formulation and implementation of Cyclic DFT is both accurate and efficient through selected examples.

The connection of cyclic symmetries with uniform bending deformations provides an elegant route to the ab-initio study of bending in nanostructures using Cyclic DFT. As a demonstration of this capability, we simulate the uniform bending of a silicene nanoribbon and obtain its energy-curvature relationship from first principles. A self-consistent ab-initio simulation of this nature is unprecedented and well outside the scope of any other systematic first principles method in existence. Our simulations reveal that the bending stiffness of the silicene nanoribbon is intermediate between that of graphene and molybdenum disulphide – a trend which can be ascribed to the variation in effective thickness of these materials. We describe several future avenues and applications of Cyclic DFT, including its extension to the study of non-uniform bending deformations and its possible use in the study of the nanoscale flexoelectric effect.

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## 1. Introduction

In recent decades, quantum mechanical calculations using Kohn-Sham Density Functional Theory (Kohn-Sham DFT) (Hohenberg and Kohn, 1964; Kohn and Sham, 1965) have become the de facto workhorse of computational materials science. The pseudopotential plane-wave method (*Plane-wave DFT*) – perhaps the most widely used implementation of the

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Kohn-Sham theory – is currently available in a number of mature software packages (Kresse and Furthmuller, 1996; Segall et al., 2002; Giannozzi et al., 2009; Gonze et al., 2002). The Plane-wave DFT approach involves expanding the unknowns (e.g., the Kohn-Sham orbitals and the electron density) into a linear combination of plane-waves<sup>1</sup>, and subsequently carrying out various computations through the use of Fast Fourier Transforms (FFTs) to seamlessly switch between quantities expressed on real space grids and their plane-wave expansion coefficients. Due to the periodic nature of plane-waves, Plane-wave DFT is well suited for the study of systems with translational symmetry. However, the study of structures which are non-periodic may require the use of large computational supercells (Martin, 2004), thereby rendering the method inefficient for such problems.<sup>2</sup>

A vast number of materials systems of interest today are non-periodic, but are associated with other physical symmetry groups. This includes for example, nanoclusters and molecules associated with point group symmetries, and helical nanostructures associated with screw transformation symmetries. The importance of such nanostructures associated with alternative (non-periodic) symmetries cannot be overstated. For instance, they are anticipated to exhibit unprecedented materials properties – particularly, collective properties such as ferromagnetism and ferroelectricity – in manners that are otherwise unavailable in the bulk phase (James, 2006). Consequently, a substantial body of work has been devoted in recent years to the theoretical framework and mathematical classification of such structures<sup>3</sup> (James, 2006; Dayal et al., 2015). Further, judicious use of the symmetries associated with these structures has been made in designing novel computational methods – both at the level of atomistic simulations (Dumitrica and James, 2007; Dayal and James, 2010; Aghaei et al., 2012) as well as electronic structure calculations (Banerjee, 2013; Banerjee et al., 2015).

While the study of electronic properties of nanostructures associated with various non-periodic physical symmetries is of much scientific and technological interest in itself, an additional outcome of having access to computational methods specifically designed to exploit the underlying physical symmetries is that these methods allow one to study the associated deformation modes. In the setting of conventional Plane-wave DFT for example, the application of a homogeneous deformation to a periodic system still results in a structure with translational symmetry, and therefore the deformed system can be easily accommodated through a unit cell that has also been deformed in the same manner. On the other hand, it is far more difficult to account for non-homogeneous deformations such as bending and torsion in the periodic setting, whereby their study (Wei et al., 2012; Naumov and Bratkovsky, 2011) is likely to involve various complications, inaccuracies and inefficiencies.

To the best of our knowledge, as far as atomistic systems are concerned, the connections between various physical symmetry groups and specific non-homogeneous deformation modes appears first in James (2006). This idea has been subsequently exploited for simulating the effects of bending deformations by means of cyclic symmetry groups (Dumitrica and James, 2007; Zhang et al., 2011; Ma et al., 2015; Koskinen and Kit, 2010b, 2010, 2012; Kit et al., 2011b), and torsional deformations by means of helical symmetry groups (Dumitrica and James, 2007; Zhang et al., 2008, 2009; Koskinen and Kit, 2010b; Kit et al., 2012, 2011, 2011b). A pervasive issue with these aforementioned works however, is that the simulations in question have been carried out within the framework of interatomic potentials or tight binding methods (classical semi-empirical or Density Functional Tight Binding (DFTB)). The failure of these more approximate models in simulating various physical systems is well known (Ismail-Beigi and Arias, 2000; Hauch et al., 1999; Cocco et al., 2010; Koskinen and Mäkinen, 2009; Naumov and Bratkovsky, 2011) and it has been understood for some time that access to a systematic self-consistent first principles simulation methodology would be highly desirable (Kit et al., 2011b; James, 2006; Banerjee, 2013). However, such a computational methodology appears to have been out of reach prior to this work.<sup>4</sup>

In view of the above discussion, we formulate and implement Cyclic Density Functional Theory (Cyclic DFT) – a self-consistent first principles simulation method for cyclic nanostructures.<sup>5</sup> Cyclic symmetries are ubiquitous in various clusters and molecular systems (Wikipedia, 2016; Hargittai and Hargittai, 2009; Willock, 2009; Go and Scheraga, 1973) (see Fig. 1 for some examples), and therefore the present methodology can be used to study a large variety of nanostructures from first principles in a systematic and efficient manner. Notably, even general point group symmetries associated with complex nanosystems usually contain cyclic groups as proper subgroups (Altmann and Herzog, 1994), which extends the scope of the various materials systems that can be studied with Cyclic DFT.<sup>6</sup> Furthermore, due to the connections between cyclic symmetries with bending deformations in nanostructures (i.e., the idea that cyclic boundary conditions locally simulate the behavior of a system subjected to uniform bending), Cyclic DFT makes it possible to carry out systematic ab-initio simulations of nanostructures subjected to bending deformations. In particular, this opens up the possibility that electro-mechanical or other multi-physics coupling effects in nanostructures can be faithfully simulated from first principles by means of this novel framework.

<sup>1</sup> Plane-waves are functions of the form  $e^{ikx}$ . They form eigenfunctions of translational symmetry operators.

<sup>2</sup> Alternatives to Plane-wave DFT include real-space methods based on finite-differences (Castro et al., 2006; Kronik et al., 2006; Ghosh and Suryanarayana; Ghosh and Suryanarayana, 2016) and finite-elements (Suryanarayana et al., 2010; J.E. Pask and Sterne, 2005; J. Pask and Sterne, 2005; Pask et al., 2001; Motamarri et al., 2013). Although these methods allow non-periodic boundary conditions to be imposed more readily, their use in general symmetry-adapted self-consistent first principles calculations has not been considered prior to this work.

<sup>3</sup> In the mechanics of materials literature, such materials systems have been referred to as *Objective Structures* (James, 2006).

<sup>4</sup> Indeed, as remarked in Kit et al. (2011b), a central difficulty has been to formulate an analog of plane-waves for non-periodic symmetries. This issue has been subsequently addressed and resolved in Banerjee (2013).

<sup>5</sup> The crystallographic restriction theorem (Senechal, 1996) prevents any periodic code – including all Plane-wave DFT codes – from making full use of the symmetry of a general cyclic structure.

<sup>6</sup> For example, the icosahedral group that is associated with many fullerenes contains a cyclic subgroup originating from a 5-fold rotational symmetry.

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