Abstract
A recent paper [J. Chem. Phys. 132 134705 (2010)] illustrated the potential of the van der Waals density functional (vdW-DF) method [Phys. Rev. Lett. 92, 246401 (2004)] for efficient first-principle accounts of structure and cohesion in molecular crystals. Since then, modifications of the original vdW-DF version (identified as vdW-DF1) has been proposed, and there is also a new version called vdW-DF2 [ArXiv 1003.5255], within the vdW-DF framework. Here we investigate the performance and nature of the modifications and the new version for the binding of a set of simple molecular crystals: hexamine, dodecahedrane, C60, and graphite. These extended systems provide benchmarks for computational methods dealing with sparse matter. We show that a previously documented enhancement of non-local correlations of vdW-DF1 over an asymptotic atom-based account close to and a few Å beyond binding separation persists in vdW-DF2. The calculation and analysis of the binding in molecular crystals requires appropriate computational tools. In this paper, we also present details on our real-space parallel implementation of the vdW-DF correlation and on the method used to generate asymptotic atom-based pair potentials based on vdW-DF.

Keywords: vdW-DF, molecular crystals, density functional theory, cage molecules, graphite, C60

1. Introduction

Supramolecular interactions such as steric hindrance, van der Waals (vdW) forces, and electrostatics play a central role in today’s biological, nano-technology, and condensed-matter research. Materials where these interactions are important can be categorized as sparse matter, since they have low electronic density in regions essential for cohesion and response. The all-pervasive vdW interactions act across such low-density regions. The need for robust computational tools that provide insight into supramolecular systems has given impetus to the development of first-principle methods that properly accounts for the binding of sparse matter.

Density functional theory (DFT) within the local density approximation (LDA) or semi-local, generalized-gradient approximations (GGA) for the exchange-correlation potential has, despite its tremendous success for dense matter, failed to consistently account for the binding in sparse matter. The van der Waals density functional (vdW-DF) method — both in the original version [2, 3], termed vdW-DF1, and in a new version, termed vdW-DF2 [4] — go beyond these local approximations by using a non-local function to approximate the correlation. Being first-principles, it deals with the vdW forces by including non-local correlations from the electron response to the dynamical field. In the vdW-DF framework the non-local correlation energy takes the form of a double-space integral:

$$E_{nl} = \frac{1}{2} \int dr \int dr' n(r) \phi(r, r') n(r').$$

The vdW-DF method inherits the excellent performance of GGAs for many dense matter systems, while extending the reach of DFT approximations to sparse matter.

The original version of vdW-DF1 has performed well for a range of systems, such as binding in molecular dimers, physisorption on surfaces, and polymer crystals [1]. Two of us have shown that it accounts for the structure of molecular crystals [5]. However, vdW-DF1 [2] overestimates binding separations by 0.2 to 0.3 Å. This has led several authors to suggest adjustments in the vdW-DF method. Using the S22 [6] data set of molecular dimers, Klimeš et al [7] optimized several GGA exchange flavors for use in place of the original choice of revPBE [8] (the x subscript indicates the exchange-part of the exchange-correlation) to the correlation in vdW-DF1; here we test optPBEx. Cooper developed an exchange flavor (C09x) for
vdw-DF1, [9] which goes like the gradient-expansion approximation (GEA) in the slowly-varying, high-density, limit. Very recently, a new version vdw-DF2 was proposed [4]. It modifies the inner functional, that vdw-DF uses to determine the local plasmon frequency $\sim q_0(r)^2$ and thereby the non-local correlation. vdw-DF2 also uses a refitted version of the PW86, [10]. This exchange functional does not induce unphysical binding effects in the exchange channel and is simultaneously less repulsive than revPBE, [11].

Computational methods designed for sparse matter benefit from using molecular crystals as testing grounds, because of the wealth of accurate experimental data on crystal structures and lattice parameters. Molecular crystals are also model system for bulk sparse matter. We therefore find it pressing to test vdw-DF2 and the suggested modifications of vdw-DF1 on these systems. Here, we extend our vdw-DF1 study of hexamine and dodecahedrane [5] with these new modifications, and include two important carbon allotropes: the C60 crystal and graphite. The latter can be viewed as a molecular crystal of graphene flakes. For the vdw-DF correlations (termed vdw-DF1c, and vdw-DF2c), we find that that both vdw-DF1c and vdw-DF2c, are considerably enhanced over a corresponding asymptotic atom-based pair potential form at, and a few Å beyond, typical binding separations.

The vdw-DF calculations for molecular crystals require an implementation that handle periodic systems; in particular, for the C60 crystal, having four molecules (240 carbon atoms) per unit cell, a moderately efficient and parallel implementation is beneficial. In this paper, we discuss some details of our parallel code for evaluating non-local correlations, in addition to discussing the method used to generate results in the asymptotic approximation (’app’).

2. Computational methods

2.1. van der Waals density functional calculations

In the vdw-DF framework, the exchange-correlation of consists of LDA correlation, GGA exchange, and the non-local correlations:

$$E^{\text{vdW-DF}}_{xc} = E^{\text{LDA}}_c + E^{\text{GGA}}_c + E^{\text{nl}}_{xc}[\mathbf{n}].$$

The total energy, $E^{\text{vdW-DF}}$, is obtained as in Refs. [5] [12] [13]. The exchange-correlation energy is evaluated non-self-consistently using the charge density, obtained in a self-consistent DFT calculation with the PBE [14] flavor of GGA (sc-GGA), utilizing the ultrasoft pseudo-potential plane-wave code DACAPO [15].

The potential energy of the crystal is the difference between the total energy in a configuration and the energy of isolated molecules: $E(a) = E^{\text{vdW-DF}}(a) - E^{\text{vdW-DF}}(a \to \infty)$. We use brute force to determine the optimal value of the unit cell dimension (denoted $a$). The molecular structure, obtained in a sc-GGA calculation, is kept constant as $a$ is varied. The experimental crystal symmetry specifies the molecular orientations [5] for all but the C60 crystal, where we use the experimental orientations [16].

A scheme using interpolation to express Eq. (1) in terms of convolutions and achieves $N \log N$ scaling has recently been reported [21]. This scheme provides a significant speedup for medium-size systems. However, the real-space version has certain merits. First, the total cpu cost remains nearly constant for any number of processors. Second, for large systems the linear scaling in system size $N$ will be important. Third, the explicit control over the integration domain is useful both in analysis of binding and for systems which are nonperiodic in some or all spatial directions; for instance, the tertiary structure of biopolymers are characteristically non-periodic. The explicit control
over scale lengths, can also be used together with coarser accounts of the vdW forces at large separations [22, 23, 20].

2.3. Generating asymptotic vdW-DF pair potentials using Bader analysis

The asymptotic atom-based pair potential approximation for the vdW energy between two molecules takes the form

\[ E_{\text{vdW-DF}} = \sum_i \sum_j \frac{C_{ij}}{|r_i - r_j|}, \]

where \( i \) and \( j \) are labels for the atoms in of the two molecules. To generate such a potential based on vdW-DF, we partition the charge density of the molecule among the atoms, using the atoms-In-Molecules (AIM) method of Bader [24], and evaluate the charge density of the molecule among the atoms, using the algorithm proposed by Henkelman et al [27], to generate Bader volumes. The molecular crystals of this study have simple structures. Hexamine and dodecahedrane forms respectively a body and face-centered cubic (bcc, fcc) with a single molecule per unit cell [5]. At low temperatures, the C60 crystal is a simple cubic, with four molecule per cell. At higher temperatures, the molecules rotate freely and the crystal becomes effectively an fcc [16]. Graphite is a layered material, with two graphene sheets stacked in an AB pattern.

Figure 3 shows the binding curve of the C60 crystal as a function of the lattice parameter \( a \) of the simple cubic. For this crystal, vdW-DF1 binds stronger than vdW-DF2, but at a larger lattice constant. The failure of DFT within GGA illustrate the need for non-local correlations to account for the binding in these crystals.

3. Crystal structure

Table 3 shows the lattice constants and cohesion energies obtained using the vdW-DF method. The lattice constants predicted by vdW-DF1 overestimates the experimental values by about 0.3 Å (per sheet for graphite), which is consistent with earlier studies [11]. The cohesion energies compares well with experimental values. The use of C09x and optPBE as exchange partner to the vdW-DF1x improves lattice constants. The former
4. Enhancement over asymptotic pair-potential form

Previous studies \cite{5,23,22} have shown that the non-local correlation of vdW-DF1 is enhanced compared to an atom-based asymptotic pair-potential (‘app’) account (Eq. 3) at binding separation and a few Å beyond. By construction ‘app’ does not include the image-plane and multi-pole effects inherent in the density-functional framework of vdW-DF. The importance of image planes were also discussed in the seminal work of Zaremba and Kohn in a surface-physics context \cite{34}. Asymptotic atom-based approximations are often used in force-field methods and in semi-empirical methods that add these interactions on top of GGA based DFT calculations (DFT-D). Since vdW-DF2 modifies the account of non-local correlation, we here investigate how this affects the enhancement over ‘app’.

Figure 5 shows the ratio between the non-local correlation and its corresponding ‘app’, \( \Delta E_{nl}/E_{app} \), for both vdW-DF1 and vdW-DF2. Because of residual noise in our determination of the \( C_6 \) coefficients, we have (< 10%) adjusted the curves to reach unity at \( d > 16 \) Å. The full (dashed) line gives the result for vdW-DF1 (vdW-DF2). Both version exhibit a significant enhancement, with the vdW-DF2 result being somewhat larger and shifted to smaller separations. The less than unity ratio at separations about 1 Å shorter than the binding separations reflects the built-in damping of the vdW forces in the vdW-DF framework; no ad hoc damping parameter needs to be introduced in the vdW-DF method.

5. Discussion and summary

The performance of variations of the vdW-DF method has been investigated for several molecular crystals. The modifications of vdW-DF1, involving only the exchange functional (C09\(_x\), optPBE\(_x\)), improves the lattice constants, but cohesion energies seem to worsen for molecular crystals. That optPBE\(_x\) did not outperform the other vdW-DF1 combinations indicate that fitting to S22, by itself, does not guarantee high precision for other types of systems. C09\(_x\) gives excellent lattice parameters. The good performance of vdW-DF2 is encouraging, pointing to higher accuracy for the vdW-DF method.

The enhancement of non-local correlation over ‘app’ shows that the nature of binding both for vdW-DF1 and vdW-DF2 differs from the asymptotic ‘app’ description. This result further questions the often used \( 1/r^6 \) atom-based approximation for van der Waals forces when used within a few Å of the binding separations \cite{5,22}.
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