Structure and binding in crystals of cage-like molecules: hexamine and platonic hydrocarbons

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In this paper, we show that first-principle calculations using a van der Waals density functional \((\text{vdW-DF})\), [Phys. Rev. Lett. 92, 246401 (2004)] permits determination of molecular crystal structure. We study the crystal structures of hexamine and the platonic hydrocarbons (cubane and dodecahedrane). The calculated lattice parameters and cohesion energy agree well with experiments. Further, we examine the asymptotic accounts of the van der Waals forces by comparing full \(\text{vdW-DF}\) with asymptotic atom-based pair potentials extracted from \(\text{vdW-DF}\). The character of the binding differ in the two cases, with \(\text{vdW-DF}\) giving a significant enhancement at intermediate and relevant binding separations. We analyze consequences of this result for methods such as DFT-D, and question DFT-D’s transferability over the full range of separations.

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I. INTRODUCTION

Understanding supramolecular structure and interactions is essential for understanding many biological processes. Biological and other supramolecular complexes as polymers and overlayers are sparse matter, that is, they contain low electronic density in essential regions. The general lack of order in these systems prohibits precise measurements of atomic structure and therefore challenges development of theoretical methods. In turn, this makes transferable first principles schemes attractive; an accurate account of simple periodic structures permits accurate characterization to be made and reliable conclusions to be drawn for more complex (non-periodic) systems. Molecular crystals and simple polymer crystals are ideal testing grounds for applications of first-principle descriptions of sparse matter. Unlike most sparse matter, they constitute ordered systems and therefore leads to unambiguous comparison between theory and experiments.

The dispersion forces underpin the cohesion of sparse matter. Modeling of sparse matter at the electronic level, therefore, requires that we take these effects into account. Traditional implementations of Density-Functional theory (DFT), which parameterizes the density functional within the local density approximation (LDA) or the generalized gradient approximation (GGA) have allowed for routine modeling of matter with dense electron distributions. However, the lack of non-local correlation and hence dispersion forces in these implementations, has effectively inhibited widespread use for general sparse matter systems. Computational methods able to predict molecular crystal structure and stability are also of value in the pharmaceutical industry, for example in mapping out competing crystalline phases for the fabrication of pharmaceuticals. The electronic structure and response are often required to understand and compute properties of technological significance. Consequently, a range of developments has aimed to extend density functional approximations with an account of dispersive interactions and thus capability to address sparse matter challenges. Such approaches include non-local functionals, inter-molecular perturbation theory, and the addition of a semi-empirical atom-based account of the dispersion forces (DFT-D). DFT-D has also been used to characterize molecular crystals.

We study molecular crystal using a van der Waals density functional \((\text{vdW-DF})\). The correlation part of this functional depends non-locally on the density and accounts for dispersion forces. \(\text{vdW-DF}\) has been used in a series of first-principle studies of sparse matter, yielding for example new insight to the twist of DNA, nanotube bundles, water hexamers, metal-organic frameworks and the binding mechanisms at organic-metal interfaces.

In this paper, we first demonstrate that \(\text{vdW-DF}\) permits structural determination of molecular crystals and second asses the character of the attractive dispersion interactions. For the first, we calculate the lattice parameters for crystals of the cage-like hexamine, dodecahedrane, and cubane molecules. For the second, we compare an atom-centered asymptotic-1/\(r^6\) approximation, frequently encountered in force-field methods, and in DFT-D, with the correlation energy provided by \(\text{vdW-DF}\). We also analyze consequences for DFT-D and question its performance at intermediate separations. The particular choice of molecules was motivated in part by their aesthetic appeal and in part for the property that their symmetric geometries permits a simple assignment and analysis of the strength of the asymptotic interactions even when expressed in terms of an atom-pair basis.

This paper has the following plan: The next section presents the molecules hexamine, cubane, and dodecahedrane and their experimental crystal structures. The third section deals with the computational details of \(\text{vdW-DF}\). The fourth gives the results for lattice parameters and bulk modulus. In the fifth section, we compare the asymptotic 1/\(r^6\)-form of van der Waals interactions with the full non-local correlation for different molecules, and the \(\text{vdW-DF}\) potential energy curve with DFT-D cal-
FIG. 1: The molecular and crystal structure of hexamine, dodecahedrane, and cubane. The upper panels show the respective molecular structures. The mid panels give schematics of the crystal structures, where the molecular symmetry and orientation are highlighted by the use of a tetrahedron, dodecahedron, and a cube in place of the molecules. The lower panel shows, for hexamine and dodecahedrane, facets of the crystal structure and for cubane the orientation of the cubane molecule in the unit cell. Hexamine has a bcc unit cell, dodecahedrane an fcc unit cell, and cubane a rhombohedral unit cell, with equal angles \( \alpha \) between the lattice vectors.

culations for a cubane dimer. The final section holds our conclusions.

II. PLATONIC MATTER

Plato asserted that the basic building blocks of Nature were five geometrical structures, today known as platonic solids. These are the five convex polyhedra with all faces, edges, and angles congruent. On the molecular level, two of these solids have synthetic hydrocarbon (compounds of only carbon and hydrogen) analogues: cubane \((C_6H_6)\), which corresponds to the cube, and dodecahedrane \((C_{20}H_{20})\), which corresponds to the twelve-faced dodecahedron. The fascination mathematicians held for these geometrical structures since antiquity echoed in the more recent struggle to synthesize their hydrocarbon representatives. The highly strained bonds posed the main challenge. Obstacles were eventually overcome and in 1964 cubane was synthesized followed by dodecahedrane in 1978. A third, tetrahedrane exists only within a larger chemical structure and no crystallographic characterization exists. Tetrahedrane does therefore not represent a good testing ground for vdW-DF and we instead study the molecular crystal of hexamine \((C_6H_{12}N_4)\). Although not a hydrocarbon, it shares several features with the platonic hydrocarbons: it is organic, its non-hydrogen atoms form a cage, and this cage has the symmetry of platonic solid tetrahedron. The top row of Fig. 1 shows the molecular structures (from left to right) of hexamine, cubane and dodecahedrane, ordered according to the ascendancy of their platonic analogues.

The second and third row of Fig. 1 show the crystal structures. The first column shows hexamine, the mid, cubane, and the final, dodecahedrane. The crystal structure of hexamine forms a bcc with a single molecule in each unit cell and \( I\bar{4}m \) symmetry. Hexamine has been used as a model system in numerous studies and the crystal structure was determined as early as in 1923. The crystal structure of cubane is rhombohedral with equal external angles and a single molecule in each cell. The molecule is oriented according to the \( R3 \) space group;
a rotation about the [111] axis specifies the configuration of the molecule. The crystal structure of dodecahedrane is face-centered cubic, also with a single molecule in each cell and Fm$ar{3}$m space group.

Hexamine finds numerous industrial uses. For instance, it serves as a component in fuel tablets and as an antibiotic. The platonic hydrocarbons find only hypothetical applications; cubane has been identified as a potential high-energy fuel and explosive.

In addition to being well-studied crystals, especially hexamine and cubane, these crystals make attractive testing grounds for vdW-DF for two more reasons. First, their simple structures allow for brute-force determination of lattice parameters. Within the crystal symmetry, this determination corresponds to mapping out the potential energy of a single parameter for hexamine and dodecahedrane, and three for cubane. The brute-force approach facilitates post-processing analysis, such as computation of bulk modulus and makes it easier to evaluate how the choice of exchange in DFT affects crystal structure and cohesion energy. Second, the high symmetry of the molecules reduces the large set of atom-to-atom interactions and can therefore account for the structure and cohesion of sparse matter. Since deconvolution of LDA: 

$E_{xc}^{vdWDF}[n] = E_c^{LDA} + E_x^{revPBE} + E_{xc}^{vdWDF}[n]$. (2)

The total energy functional of vdW-DF, $E_{xc}^{vdWDF}[n]$, also includes the standard electrostatic and kinetic-energy terms within the Kohn-Sham scheme. It is convenient to write this energy in terms of a semi-local part $E_0[n]$ containing all but the non-local correlation, so that $E_{xc}^{vdWDF}[n] = E_0[n] + E_{xc}^{nl}[n]$. For input charge density $n(r)$, we use the result of semi-local calculations with the PBE flavor of GGA. We will refer to calculations with the PBE flavor of GGA as DFT-GGA. The charge density could also have been obtained within fully self-consistent vdW-DF. However, the two-step non-self-consistent procedure introduces only a slight approximation. Previous studies have documented that for systems with small charge transfer, binding energies of non-self consistent vdW-DF only differ by tiny amounts from fully self-consistent energies.

To speed up evaluation of the non-local correlation, we introduce a radius cutoff based on the decay of van der Waals forces at large separations. With this cutoff, the kernel takes form

$$E^{nl}_c[n] \approx \frac{1}{2} \int_{V_0} \int_{|\mathbf{r} - \mathbf{r}'| < R} \mathbf{r} n(\mathbf{r}) \int_{|\mathbf{r} - \mathbf{r}'| < R} \mathbf{r}' \phi(\mathbf{r}, \mathbf{r}') n(\mathbf{r}') \, \text{d} \mathbf{r} \, \text{d} \mathbf{r}' \, \phi(\mathbf{r}, \mathbf{r}') n(\mathbf{r}') \, \text{d} \mathbf{r} \, \text{d} \mathbf{r}' \, \phi(\mathbf{r}, \mathbf{r}') n(\mathbf{r}') \, \text{d} \mathbf{r} \, \text{d} \mathbf{r}' \, \phi(\mathbf{r}, \mathbf{r}') n(\mathbf{r}') \, \text{d} \mathbf{r} \, \text{d} \mathbf{r}' \, \phi(\mathbf{r}, \mathbf{r}') n(\mathbf{r}') \, \text{d} \mathbf{r} \, \text{d} \mathbf{r}' \, \phi(\mathbf{r}, \mathbf{r}') n(\mathbf{r}') \, \text{d} \mathbf{r} \, \text{d} \mathbf{r}' \, \phi(\mathbf{r}, \mathbf{r}') n(\mathbf{r}') \, \text{d} \mathbf{r} \, \text{d} \mathbf{r}' \, \phi(\mathbf{r}, \mathbf{r}') n(\mathbf{r}') \, \text{d} \mathbf{r} \, \text{d} \mathbf{r}' \, \phi(\mathbf{r}, \mathbf{r}') n(\mathbf{r}') \, \text{d} \mathbf{r} \, \text{d} \mathbf{r}' \, \phi(\mathbf{r}, \mathbf{r}') n(\mathbf{r}') \, \text{d} \mathbf{r} \, \text{d} \mathbf{r}' \, \phi(\mathbf{r}, \mathbf{r}') n(\mathbf{r}') \, \text{d} \mathbf{r} \, \text{d} \mathbf{r}' \, \phi(\mathbf{r}, \mathbf{r}') n(\mathbf{r}')$.

In the above expression, we see that the CPU-cost for evaluating the non-local part of vdW-DF goes as $R^4O(V_0)$. Thus, for large or periodic systems the computational costs increase linearly with system size. To cut computational costs further, we introduce an extra radius cutoff corresponding to the separation between dense and sparse sampling of the charge-density grid. We note that Ref. 54 reports a more elaborate scheme which considerably reduces CPU-costs, yet our simple measure was sufficient for our non-self consistent calculations as the underlying DFT-GGA calculations of electronic density dominated time consumption.

The use of revPBE for exchange in vdW-DF was motivated by the fact that this exchange functional excludes unphysical binding effects at large distances.

For a range of systems, vdW-DF overestimates binding separations. Several studies indicate that this discrepancy can be attributed to the details of the exchange functional. Puzder et al. have demonstrated that replacing Hartree-Fock exchange with revPBE improves binding separations for benzene dimers. Gulans et al. have shown that for a selected range of molecular complexes the PBE exchange functional improves binding energies. We furthermore illustrate the sensitivity to exchange by including results based on use of an alternative vdW-DF(PBE), where revPBE exchange has been replaced by that of PBE. We do not argue for replacing vdW-DF with vdW-DF(PBE), instead we simply explore consequences of a different account of exchange.

To calculate crystal parameters and cohesion energy, we minimize the potential energy. In many respects this vdW-DF structure determination is similar to those in Refs. 21,46. The potential energy is given by the difference between the total energy of the full crystal and
a reference energy for a system of isolated molecules 

\[ E_{\text{coh}}(a, \{\alpha\theta\}) = E^{\text{vdW-DF}}(a, \{\alpha\theta\}) - E^{\text{vdW-DF}}(a \to \infty, \{\alpha\theta\}). \]  

(4)

In the above equation the curly brackets are specific for the cubane crystal as it depends on three rather than one parameter. In the reference calculation corresponding to the reference energy, \( E^{\text{vdW-DF}}(a \to \infty, \{\alpha\theta\}) \), the semi-local part is obtained somewhat differently from the part containing the non-local correlation. For the former, we effectively isolate the molecules in our periodic boundary calculations, by using a unit cell of doubled size in all directions. This measure secures negligible charge overlap between the molecules in the supercells. For the latter (nonlocal) part we restrict the integral of Eq. (3) to the central supercell to avoid coupling between the enlarged unit cells. Hence, only non-local correlations within the molecule contribute to the reference energy.

To enhance accuracy in the evaluation of the non-local part of the potential energy, we systematically cancel a small, but noticeable, grid dependence in the evaluation of Eq. (3) This cancellation is performed by making sure to use the same FFT grid spacing in the reference calculation as in the main calculation. Furthermore, we make sure to place the isolated molecules in the same relative configuration to the underlying grid in the reference calculation as in the main calculation. We thus perform an additional reference calculation for every molecular configuration investigated. These measures have been used to secure a high accuracy of the non-local part of vdW-DF in several earlier studies.

We map the potential energy landscape by varying the lattice parameters of the molecular crystals within the experimental crystal symmetry. The stiff cage-molecules allow us to keep the internal coordinates of the molecules frozen for all configurations. The molecular structures are determined in isolation using the PBE flavor of GGA. The resulting bond lengths will be compared with experimental data in the next section to verify the utility of conventional DFT-GGA for the internal structure of strained molecules.

### TABLE I: Experimental and calculated bond lengths of hexamine, cubane, and dodecahedrane.

| Parameter          | Hexamine | Cubane | Dodecahedrane |
|--------------------|----------|--------|---------------|
| \( l \) [Å]       | 1.472    | 1.566  | 1.549         |
| \( E^{\text{coh}} \) [Å] | 1.476\(^a\) | 1.562\(^b\) | 1.544\(^c\) |
| \( l_{\text{C-H}} \) [Å] | 1.101    | 1.095  | 1.100         |
| \( E_{\text{C-H}}^{\text{coh}} \) [Å] | 1.088\(^a\) | 1.097\(^b\) | -             |

\(^a\) Ref. 58  
\(^b\) Ref. 59  
\(^c\) Ref. 60

### TABLE II: The vdW-DF prediction of lattice parameters, cohesion energy and bulk modulus for the crystals of hexamine, cubane and dodecahedrane compared with experimental values.

| Parameter | Hex. | Cub. | Dod. |
|-----------|------|------|------|
| \( a \) [Å] | 7.14 | 5.45 | 10.92 |
| \( E_{\text{coh}} \) (eV) | -1.0127 | -0.77 | -1.46 |
| \( B_0 \) (GPa) | 10.0 | 7.2 | 12.2 |

| Parameter | Exp. | vdW-DF | vdW-DF (PBE) |
|-----------|------|--------|--------------|
| \( a \) [Å] | 6.93 | 6.910\(^a\) | -            |
| \( E_{\text{coh}} \) (eV) | -1.427 | -0.827\(^b\) | -            |
| \( B_0 \) (GPa) | 14.0 | 7.0\(^c\) | -            |

\(^a\) Ref. 58  
\(^b\) Ref. 59  
\(^c\) Ref. 60

The electronic-structure calculations rely on the plane-wave code DACPO\(^d\) using ultra-soft pseudopotentials. In combination with a separate reference calculation as previously discussed, we secure the convergence of the non-local correlation by specifying an FFT-grid spacing less than 0.13 Å. This spacing leads to an effective plane-wave energy cutoff of at least 500 eV. For all crystals, we set the Monkhorst-Pack \( k \)-sampling to \( 4 \times 4 \times 4 \).

### IV. STRUCTURE DETERMINATION

#### A. Molecular structure

Table I shows the calculated molecular structures. It demonstrates DFT-GGA can account for the intramolecular bonding even in the highly strained cubane molecules. The resulting bond lengths differ by less than 1 % from the experimental values. In first principle studies of molecular crystals, accurate determination of lattice parameters require accurate account of constituent molecules.

Unlike many calculations, where determination of crystal structure often starts from the structure of the individual molecules, most experiments resolve the molecular structure by looking at the diffraction pattern of a full molecular crystal. For our purposes of testing the first-principle vdW-DF method, this is fortunate, as efforts to characterize molecular structures also generate an abundance of experimental data on molecular crystal structures.
FIG. 2: The potential energy curves for the crystal of hexamine and dodecahedrane (left panel) and corresponding contour plots for the crystal of cubane (right panel). The left panel shows potential energy where the curves are normalized separately so that the experimental lattice parameter and the calculated cohesion energy equals unity. The solid curve represents dodecahedrane and the dashed hexamine. The difference in the optimal $a/a_{\text{exp}}$ value can be attributed to the experimental lattice parameter being measured at low temperature for hexamine, but not for dodecahedrane. The right panel shows spline-interpolated contour plots of the two-dimensional intersection of the three-dimensional potential energy landscape. The main figure corresponds to the optimal value of the internal angle $\theta$, while the insert corresponds to the optimal value of the unit cell length $a$. The pronounced asymmetry of the curves and contours reflect the hard wall provided by Pauli repulsion.

B. Crystal structure

Figure 2 shows the binding curves and contours found by varying the molecular crystals’ lattice parameters identified in Fig. 1. The simple crystal structures of hexamine and dodecahedrane give a one-dimensional potential energy landscape, while the cubane crystal has a three dimensional one. In the right panel of Fig. 2, we display the $a\alpha$ and the $a\theta$ intersections, for the optimal values of $\theta$ and $a$. The curves exhibit a pronounced asymmetry around their minimum. This asymmetry arise because the van-der Waals attraction is much softer than the kinetic-energy repulsion.

Table II contains the calculated results and experimental values. Standard vdW-DF performs well both for lattice parameters and cohesion energy. If not directly available, we obtain experimental cohesion energies by correcting for gas phase and vibrational contributions to the enthalpy of sublimation, using the method described in Refs. 65,66.

The bulk modulus is obtained with use of polynomial interpolation according to the scheme of Ziambaras and Schröder. 44 The required polynomial were constructed using data from selected one-dimensional deformations. 67 For hexamine, where the experimental bulk modulus is available, the computed value show fair agreement with the experimental value. There is also a trend for bigger cage molecules to have a larger bulk modulus. We attribute this trend to the fact that for bigger molecules a smaller relative part of the unit cell consists of soft intramolecular regions. Therefore, as the relative unit cell dimensions change, the distance between (stiff) molecules changes more for big molecules than for small molecules.

For all three crystals, we find unit-cell volumes somewhat larger than the experimental ones. Similar over-estimations have also been encountered in previous studies. 21,46,55 The alternative choice of PBE as exchange functional, vdW-DF(PBE), influences results substantially. On one hand, it improves lattice parameters, almost to level of standard DFT for intra-molecular bonds. On the other hand, the value of cohesive energy and bulk modulus worsens. These results signal that the main discrepancy between experiments and vdW-DFT stems from the specific form of semi-local exchange. 21,53–55

We note that an ab initio study of cubane has previously been performed at the LDA level. 68 Being a local functional, LDA has no physical basis for the van der Waals binding that provides the cohesion of this molecular crystal. The spurious LDA binding arises from an unphysical accounts of exchange. Being a local functional, LDA has no physical basis for the van der Waals binding that provides the cohesion of this molecular crystal. The spurious LDA binding arises from an unphysical accounts of exchange. 46,52 Once the molecular crystals are investigated with DFT-GGA, which has an improved account of exchange, the binding essentially vanishes. 68

V. ASYMPTOTIC PAIR POTENTIALS VERSUS NON-LOCAL CORRELATION

The asymptotic van der Waals interactions between two atoms or molecules goes as the simple power law $C_6/r^6$, where $C_6$ gives the strength of the interaction. This familiar result can be derived from second-order perturbation theory or from an analysis of the shifts in the zero-point motions of the electron. A common strategy in force-field methods and empirical extensions of DFT
is to adopt such an asymptotic form at all separations in terms of atom-centered pair-potentials (APP). However, we cannot take for granted that the asymptotic behavior should hold for separations closer to that of intramolecular binding. On the contrary, because van der Waals forces arise from correlated motion of electrons and not from the atomic nuclei, several mechanisms affect and enhance the interaction at short and intermediate separations; higher order moments contribute, polarizability changes as charge is distorted and finite-k dispersion of the electronic response becomes important. Zaremba and Kohn considered adsorption of noble atoms on surfaces and documented a significant enhancement of dispersion energies over an atom-centered account; their asymptotic $1/d^3$ form use the distance to an image plane $d$, rather than to the surface atoms. Within vdW-DF, Kleis et al. demonstrated that for interactions in nanotube bundles, the force stems primarily from the electron tail around the nanotube, and that as the tubes get closer, higher order moments dominate over the asymptotic interaction. Part of this enhancement can be interpreted as an image-plane effect.

Here we investigate whether an atom-centered $1/r^6$ form is a good approximation for the non-local correlation of molecular dimers. As our argument is based on the asymptotic vdW-DF account of van der Waals forces, we also discuss for these molecules the accuracy of the asymptotic account. In the first subsection, we compare the non-local correlation of vdW-DF for dimers of hexamine, cubane, and dodecahedrane with its corresponding atom-centered pair potentials. We document a significant enhancement of the non-local correlation at short (binding) separations and at intermediate separations, one to three Ångström beyond typical binding separations. In the second subsection, we discuss the accuracy of our $C_6$ coefficients. In the third, we investigate consequences of this result, in particular for the use of DFT-D. We will argue that although standard DFT-D methods can provide good descriptions of both short and asymptotic separations, their asymptotic atom-centered form does not describe the enhancement of correlation at intermediate separations exhibited by vdW-DF.

A. Asymptotic vdW-DF

For the the asymptotic van der Waals forces, the $C_6$ coefficient between two fragments, $A$ and $B$, can be computed from the general formula

$$C_6^{AB} = \frac{3}{\pi} \int_0^\infty du \alpha_A(iu)\alpha_B(iu),$$

where $\alpha(\omega)$ is the polarizability of the fragment. In order to calculate the $C_6$ coefficients we approximate $\alpha(\omega)$ with the local external-field susceptibility of vdW-DF,

$$\chi_A^{vdW-DF}(\omega, r) = \frac{n_A(r)}{[9\rho_0(r)^2/8\pi]^2 - \omega^2},$$

and a polarizability given by

$$\alpha_A^{vdW-DF}(\omega) = \int d^3r \chi_A^{vdW-DF}(\omega, r).$$

To generate vdW-DF based atom-centered pair potentials (APP-vdWDF), we first partition the full charge density $n(r) = \sum_i n_i(r)$ among the atoms of the molecules with aid of Bader analysis. Based on this charge partition, we calculate the atom-to-atom $C_6$ coefficients using Eq. (5). Initially, this procedure generates $N^2$ different $C_6$ coefficients for a molecular dimer of $N$ atoms per molecule. For a dodecahedrane dimer, we get as much as $40 \times 40 = 1600$ coefficients. Fortunately, because of the high symmetry of the isolated molecules,
this number reduces to only three equivalent values for
cubane and dodecahedrane: \(C_{C-C}^6\), \(C_{C-H}^6\), and \(C_{H-H}^6\). For
hexamine, the extra nitrogen atoms lead to six co-
efficients. As noise in the electronic density affects the
value of the coefficients, we average over a large set of
equivalent values to obtain the final values.

TABLE III: Computed values of the \(C_6\) coefficients (Hartree
atomic units) for different pairs of atoms within respective
molecules, using the asymptotic form of vdW-DF with charge
density as partitioned with a Bader analysis. The figure also
shows the molecule-molecule \(C_6\) coefficients obtained with
the Anderson-Langreth-Lundqvist (ALL) scheme and the
molecule-molecule \(C_6\) coefficients obtained with the use of pa-
rameters given in DFT-D schemes.

\[
C_6^{\text{vdWDF}} \quad \text{hex} \quad \text{cub} \quad \text{dod}
\]
\[
\begin{array}{ccc}
C-C & 4.44 & 13.5 & 11.2 \\
C-H & 4.04 & 6.87 & 6.45 \\
H-H & 3.98 & 3.72 & 4.07 \\
N-N & 32.6 & - & - \\
N-C & 12.0 & - & - \\
N-H & 11.0 & - & - \\
\text{mol-mol (vdW-DF)} & 3470 & 1990 & 11300 \\
\text{mol-mol (ALL)} & 3270 & 1940 & 10200 \\
\text{mol-mol (Wu)} & 4340 & 2600 & 16300 \\
\text{mol-mol (Grimme)} & 4000 & 2630 & 16400 \\
\text{mol-mol (Jurečka)} & 4790 & 3120 & 19500 \\
\end{array}
\]

The upper part of Table III shows the \(C_6\) coefficients
calculated within asymptotic vdW-DF, both as partitioned
according to the Bader analysis and as evaluated
for the entire molecule. The calculated coefficients per
atomic pair deviates much from a naive assignment of
the full coefficient of the molecule according to the num-
ber of valence electrons of the underlying atom. In such a
scheme the C-C coefficient would be 16 times larger than
the H-H coefficient, while in fact, for cubane and dodec-
ahedrane, it is merely three-four times stronger. This re-
result can be attributed to the relative stronger response of
the low-density regions surrounding the hydrogen atoms
as \(\eta_0(r) \propto [n(r)]^{1/3}\) (in the homogeneous limit), and these
areas dominate \(E_6^{\text{all}}\). The somewhat anomalous values for
hexamine can be attributed to our Bader analysis scheme
partitioning a significant portion of the charge density
near the carbon atoms to the centrally located nitrogen
atoms. For cubane and dodecahedrane the partitioning
was similar, and the differences in atomistic \(C_6\) values
show that they are influenced by their local environmen.

Having generating \(C_6\) coefficients appropriate for a
comparison between the asymptotic account and the
full correlation of vdW-DF, we study dimers of hexam-
line, cubane and dodecahedrane at different separations.
We choose orientations that are given by the nearest-
neighbor configurations in the crystals. The total asym-
ptotic non-local correlation of APP-vdWDF reads
\[
E_{\text{app}}^{\text{vdWDF}} = \sum_i \sum_j \frac{C_{ij}^{(0)}}{|r_i - r_j|},
\]
where \(i\) and \(j\) label atoms in separate molecules of the dimer.

Figure 3 shows results for the full non-local correla-
tion of vdW-DF (solid curve) and that of APP-vdWDF
(dashed curve). At large separations these two curves
converge. In contrast, they differ significantly at relevant
binding (short) separations and at intermediate separa-
tions. At these separations the non-local correlation is
almost double as large as that of APP-vdWDF, for both
hexamine and cubane, while for the biggest molecule, do-
decahedrane, the difference is smaller. For all dimers, we
also need to go to relatively large separations to recover
asymptotic values for the non-local correlation.

As vdW-DF is an \textit{ab initio} functional, based on a set of
exact sum rules\textsuperscript{22} the strong enhancement of non-local correlations at short and intermediate separations indi-
cates that the asymptotic form neglects important contri-
butions. It also highlights that in constructing modified
semi-empirical van der Waals functionals\textsuperscript{19} a fitting
of the asymptotic functional to \(C_6\) coefficients does not
guarantee an accurate description at short binding sepa-
ration.

B. Comparison of \(C_6\) coefficients

The lower part of of Table III gives the molecu-
lar \(C_6\) coefficients calculated with asymptotic vdW-DF,
the Anderson-Langreth-Lundqvist (ALL) scheme\textsuperscript{24} and
computed using the atomic coefficients of Wu et al.
Grimme\textsuperscript{25} and Jurečka et al.\textsuperscript{26} The ALL and vdW-
DF give coefficients smaller than that used in DFT-D
schemes.

We expect that Grimme and Wu provide good values
for molecular \(C_6\) coefficients, because their underlying
atomistic coefficients were fitted to reproduce a range of
accurate molecular \(C_6\) coefficients calculated from experi-
mental molecular polarizabilities (Ref. 16 and refer-
ences therein). The coefficients of Jurečka\textsuperscript{27} give some-
what larger molecular \(C_6\) coefficients. This comes from the
use of Slater-Kirkwood average\textsuperscript{28} for \(C_6\) coefficients
between different atomic species, while keeping those of
Grimme for indentical atomi species (the \(C_6\) coefficents
of Grimme are optimized for a different average.
Asymptotic vdW-DF and ALL likely underestimates the
\(C_6\) coefficients for these molecules; they are 20-30 %
smaller than that used in DFT-D methods. For the sim-
ilar ALL scheme, Ref. 17 reports an underestimation of
\(C_6\) coefficients for larger molecules, in particular for ben-
ze and C60. A difference between the ALL scheme and
asymptotic vdW-DF is that for the former a hard cutoff
accounts for plasmon damping, while for the latter, the
local response \(q_0(r)\) provides a smooth cutoff. There is
good consistency between the two methods. Both methods also assume a local, scalar, relationship between the applied and the full electric field, which is an approximation for finite-sized objects. We speculate that this approximation contributes to the underestimation of $C_6$ coefficient for the investigated, relatively large, molecules.

| TABLE IV: Atomistic $C_6$ coefficients for cubane used in APP-vdWDF (calculated with asymptotic vdW-DF and charge density partitioned with Bader analysis), and coefficients used in DFT-D methods. |
|-----------------|-----------------|-----------------|-----------------|
| $C_6^{\text{vdWDF}}$ | vdW-DF | Wu$^a$ | Grimme$^b$ | Jurečka$^c$ |
|-----------------|------------------|------------------|------------------|------------------|
| C-C | 13.5 | 22.06 | 28.3 | 28.3 |
| C-H | 6.8 | 7.89 | 5.01 | 8.82 |
| H-H | 3.7 | 2.83 | 2.75 | 2.75 |

$^a$Ref. 16 $^b$Ref. 17 $^c$Ref. 18

Table IV shows atomistic $C_6$ coefficients for cubane as calculated with asymptotic vdW-DF, and given by Wu$^a$, Grimme$^b$ and Jurečka$^c$ for use in DFT-D schemes. vdW-DF weights the relative response of the carbon less than that of the hydrogen, compared with the values of DFT-D. This property could relate to the above mentioned approximate treatment of electrodynamics. It could also relate to the carbon atoms being located somewhat inside the molecule, having a different local charge density and responding less to external fields than an atom on the exterior would; in contrast, DFT-D does not discriminate between atoms at different locations.

C. Consequences for atom-based pair potentials: the binding curve of cubane

The vdW-DF results presented in the first subsection show that a simple asymptotic account only partially captures correlation effects at short and intermediate separations. As DFT-D use such an asymptotic form to describe non-local correlations, this result stands in apparent contrast to the many successful applications of DFT-D.$^{16,18,78,80}$

To understand consequences of our result for methods such as DFT-D, we must first consider other effects that could contribute to the difference between APP-vdWDF and the non-local correlation of vdW-DF. In vdW-DF, correlations are described by $E_{\text{coh}}^{\text{LDA}} + E_{\text{nl}}^{\text{vdW}}$ and hence $E_{\text{coh}}^{\text{LDA}}$ also accounts for semi-local correlations.$^{10,45}$

Second, we must consider the specific designs of actual DFT-D schemes, because these could counteract the lack of enhancement of non-local correlations. To describe exchange-correlation, DFT-D combines the asymptotic atom-centered form with a semi-local GGA account. It also introduces fitting parameters to be used in combination with a specific GGA flavors.

The top panel of Fig. 4 shows that gradient corrections do not account for the difference between the full vdW-DF and the APP-vdWDF results. For APP-vdWDF, we can combine the purely semi-local correlation of PBE with APP-vdWDF (in a new description APP-mod),

$$E_{\text{APP-mod}}^{\text{vdWDF}}(d) = E_{\text{APP-vdWDF}}^{\text{vdWDF}}(d) + \Delta E_{\text{PBE}}(d) - \Delta E_{\text{LDA}}(d),$$

(9)

to assess the magnitude of purely semi-local corrections relative to the difference between vdW-DF and APP-vdWDF. In this APP account, we have introduced the LDA and PBE terms: $\Delta E_c(d) = E_c(d) - E_c(d \to \infty)$.

We focus our discussion on the cubane dimer. The lower thin solid curve gives APP-mod; the thick solid curve gives the non-local correlation of vdW-DF. The curves are shown as a function of the intermolecular distance $d$, with $d_0$ indicating the vdW-DF binding distance in the crystal. At short separations, the thin curve lies closer to the thick curve than the corresponding APP-vdWDF result (thick dashed curve). Thus, some of the difference between APP-vdWDF and the non-local correlation arises from a lack of semi-local correlation contributions in APP-vdWDF.$^{10}$ However, even with this inclusion the difference is still significant, and at intermediate separations it remains undiminished.

The middle panel of Fig. 4 details the effects of using the semi-empirical fitting of DFT-D and the larger $C_6$ coefficients. We compare the binding curve for cubane obtained by use of vdW-DF with the binding curve obtained with DFT-D calculations. We select the schemes of Grimme$^{17}$ and Jurečka$^{18}$ as these provide parameters for the PBE flavor of exchange-correlation, which is available to us.$^{81}$

The DFT-D scheme of Grimme scales the strength of the dispersive interaction to a particular semi-local exchange-correlation to achieve good performance at short separations. For the PBE flavor of GGA, the cohesion energy of a dimer reads

$$E_{\text{coh}}^{\text{DFT-D,G}} = E_{\text{coh}}^{\text{PBE}} + s_6 \sum_{ij} j_{\text{PBE,G}}^{ij} \left( |r_i - r_j| \right) \frac{C_6^{ij}}{|r_i - r_j|^6},$$

(10)

where $s_6 = 0.7$. This scheme therefore sacrifices the asymptotic description in favor of the a good description of binding separations. The scheme of Jurečka instead adjust parameters of the damping function to the flavor of semi-local exchange-correlation,

$$E_{\text{coh}}^{\text{DFT-D,J}} = E_{\text{coh}}^{\text{PBE}} + \sum_{ij} j_{\text{PBE,J}}^{ij} \left( |r_i - r_j| \right) \frac{C_6^{ij}}{|r_i - r_j|^6},$$

(11)

and ensure that $j_{\text{PBE,J}}^{ij} \to 1$ for large separations. The DFT-D scheme can therefore, in principle, describe both asymptotic and binding separations. However, the question remains on how it performs for systems where characteristic separations lies between these two limits.

The binding curves of vdW-DF(revPBE) (the solid curve) and for the DFT-D scheme of Grimme(PBE) (up-
Our results suggest that APPs and DFT-Ds could be improved at intermediate separations. A possible strategy is to replace the atomic separations \( r \) by an effective separation \( r - r_0 \), where \( r_0 \) reflects the image-planes found for nanotubes and surfaces in Refs. \[23,71\]. Keeping this (surface-physics) effect would increase the strength of the dispersion interactions at shorter separations.

In summary, the results of this section suggests that an asymptotic atom-based pair potentials has a limited transferability over the full range of separations. Thus, for schemes using such a form, our results raises questions on their ability to generate accurate results under broad condition (having multiple characteristic separations), for instance involving phase transitions or processes that drive the system out of equilibrium, in protein unfolding, in phase transitions, or simply for systems which have competing interactions.

We note that there is no guarantee that vdW-DF, in its current form, can provide an accurate account under such broad conditions. A vdW-DF limitation is here exemplified by the likely underestimation of \( C_6 \) coefficients for the platonic molecules. Nevertheless, we argue that non-local functionals, like vdW-DF, hold the most promise for dealing with molecular configurations under broad conditions. This is because an electron-based approach provides a framework which naturally includes image-plane and multipole effects. It therefore holds the key to an account which describe the variation in dispersive response over the full range of separations.

VI. CONCLUSIONS

For the three cage-like organic molecular crystals, hexamine, cubane and dodecahedrane, vdW-DF gives lattice
parameters and cohesion energy that agree well with experiments, although for all three crystals the unit cell volumes are overestimated. A substantial sensitivity of lattice parameters and cohesion energy to the flavor of semi-local exchange signals that this overestimation stems mostly from the chosen form of exchange functional.

We have also shown that, at short and intermediate separations, the full non-local correlation of vdW-DF is considerably larger than its corresponding atom-based asymptotic account. Notwithstanding that the asymptotic account of vdW-DF likely needs improvement, this enhancement indicates that the asymptotic $1/r^6$ form of atomic pair potentials, by construction, can not give a transferable account over a large range of separations.

This paper underlines the usefulness of studying simple model sparse systems as molecular crystals to gain insight into methods intended for the study of sparse and supramolecular systems. Both DFT-D and vdW-DF benefit from such testing, because they are designed to be parameter-free, and an accurate account of molecular crystals would suggest an accurate account of more complex assemblies of similar molecules. The presented molecular crystals provide particularly accessible cases of extended systems and can therefore be used in conjunction with future development of pair-potential methods and exchange-correlation functionals.

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