Improved description of the structure of molecular and layered crystals: Ab-initio DFT calculations with van der Waals corrections.

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Abstract

The implementation of appropriate techniques for full structural optimizations of periodic systems in the DFT-PAW package VASP, including lattice parameters and atomic positions relaxations together with a correction that allows an appropriate modelling of London dispersion forces, as given by the DFT+D2 approach of Grimme [J. Comp. Chem. 27, 1787 (2006)] is reported. Benchmark results on a series of prototype systems are presented and compared to results obtained by other methods and experimental data. It is demonstrated that the computationally inexpensive DFT+D2 scheme yields reasonable predictions for the structure, bulk moduli, and cohesive energies of weakly bonded materials.

Keywords: London dispersion forces, lattice optimization, DFT, DFT+D, PAW, electronic structure of solids

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I. INTRODUCTION

Density functional theory (DFT) has become an important tool in investigating the structure of various types of materials [1-5]. While in small molecular systems it is the chemical bonding between nearest neighbors which determines the structure, with increasing size of the systems, and in particular in molecular assemblies, weak intermolecular forces start to play a more-and-more determining role. This is particularly true in crystalline molecular materials, which are held together either by electrostatic and polarization interactions or, in their absence or in case of their weaker intensity, by London dispersion forces.

In order to cope with this challenge, theory should have at its disposal not only appropriate total energy functionals, which take into account correctly these weak intermolecular forces, but also adapted tools to perform geometry optimizations on shallow potential energy surfaces with many local minima, which allow us to optimize not only atomic positions but also the lattice/cell parameters in crystalline materials.

Popular density functionals are unable to describe correctly van der Waals interactions resulting from dynamical correlations between fluctuating charge distributions [6] and therefore they are intrinsically unadapted to optimize lattice parameters in molecular materials. In spite of the considerable progress achieved in this domain during the recent few years [7], a fully ab initio treatment of the dispersion forces is still too expensive to become a routine tool for larger systems. Pragmatic method to work around this problem has been given by the DFT+D approach [8], which consists in adding a semiempirical dispersion potential to the conventional Kohn-Sham DFT energy. Among the numerous attempts to provide a consistent parameterization, which is compatible with the exchange-correlation functional, the approach of Grimme [9-11] seems to be one of the most successful. In this method van der Waals interactions are described via a simple pair-wise force field, which is optimized for popular DFT functionals including PBE [12] and B3LYP [13, 14]. The performance of the method for optimization of some extended systems has been tested recently by other researchers, see e.g. Refs. [15-19]. After completion of our work, Grimme and his coworkers published a considerably more sophisticated parameterization, called DFT+D3 [20]. In the present article we focus on the previous version [10], referred to as DFT+D2.

Here we describe our implementation of Grimme's DFT+D2 approach in the popular solid-state PAW code VASP [21-24], including not only atomic forces but stresses on the unit
cell, making possible full geometry relaxations, including cell volume and shape optimization. Full relaxation of molecular crystal structures has been attempted by Ferenczy et al. [25, 26] by semiempirical model Hamiltonians combined with an empirical force field. The general framework for full structural optimizations of periodic systems has been discussed in [27].

In the present study we test the performance of Grimme’s DFT+D2 method for the optimization of atomic and lattice degrees of freedom on a set of selected extended systems. In the following section the reader finds a brief description of the methodology, including working expressions for the calculation of stresses. Section III describes results for various classes of materials, where London dispersion forces are expected to play a significant role: rare gas solids, molecular crystals, layered materials and finally some covalently bound and partially ionic systems. The main conclusions are presented in Section IV.

II. METHODOLOGIES

A. Electronic structure calculations

Periodic DFT calculations have been performed using the VASP code [21–24]. The Kohn-Sham equations have been solved variationally in a plane-wave basis set using the projector-augmented-wave (PAW) method of Blöchl [28], as adapted by Kresse and Joubert [29]. The exchange-correlation energy was described by the functional of Perdew, Burke and Ernzerhof (PBE) [12] based on the generalized gradient approximation. Computational details such as plane wave cutoff and Brillouin zone sampling are discussed for each system separately in Sec. III. For all the computations presented in this paper, standard PAW data sets have been used.

B. Dispersion energy correction

The van der Waals interactions have been computed using the semiempirical correction of Grimme [10]. In this method, the total energy of the system is defined as a sum of the self-consistent Kohn Sham energy ($E_{KS,DFT}$) and a semiempirical correction ($E_{disp}$):

$$E_{DFT+D} = E_{KS,DFT} + E_{disp}. \quad (1)$$
The dispersion energy for periodic systems is defined as

\[ E_{\text{disp}} = -s_6 \sum_{i=1}^{N_{\text{at}}} \sum_{j=1}^{N_{\text{at}}} \sum_{L \neq 0} C_{ij}^{6} \frac{f(|r_{i,0} - r_{j,L}|)}{|r_{i,0} - r_{j,L}|^6}, \]  

(2)

where summations are over all atoms \( N_{\text{at}} \) and all translations of the unit cell \( L = (l_1, l_2, l_3) \), the prime indicates that \( i \neq j \) for \( L = 0 \), \( s_6 \) is a global scaling factor, \( C_{ij}^{6} \) denotes dispersion coefficient for atom pair \( ij \), \( r_{i,L} \) is a position vector of atom \( i \) after performing \( L \) translations of the unit cell along lattice vectors. The term \( f(r_{ij}) \) is a damping function

\[ f(r_{ij}) = \frac{1}{1 + e^{-d(r_{ij}/R_{ij} - 1)}}, \]  

(3)

whose role is to scale the force field such as to minimize contributions from interactions within typical bonding distances. Combination rules for dispersion coefficients \( C_{ij}^{6} \) and vdW radii \( R_{ij} \) are

\[ C_{ij}^{6} = \sqrt{C_{i}^{6}C_{j}^{6}}, \]  

(4)

and

\[ R_{ij} = \frac{1}{2} (R_{i} + R_{j}), \]  

(5)

respectively.

All force field parameters were set as proposed in Ref. [10] for PBE functional: \( s_6 = 0.75, d = 20 \), values of \( C_{i}^{6} \) and \( R_{i} \) are compiled in Tab. I. In principle, the summation \( \sum_{L} \) in eq. 2 should run over all possible (i.e. infinitely many) translations of the unit cell. In practice, however, terms corresponding to interactions over distance longer than a certain suitably chosen cutoff radius contribute only negligibly to \( E_{\text{disp}} \) and can be ignored. In this study, the value of cutoff radius was set to 40 Å.

C. Dispersion energy gradients

Most of modern optimization algorithms use potential energy gradients to optimize geometry of the system. In this section we briefly discuss calculation of all quantities needed for full structural optimization of periodic systems: energy derivatives with respect to atomic positions, and derivatives with respect to components of lattice vectors.
Let the structure of a periodic system be characterized by three lattice vectors, arranged in the matrix \( \mathbf{h} = [a_1, a_2, a_3] \) and by the 3N fractional coordinates, \( s = \{s_a^\alpha\} \) defined as:

\[
s_a^\alpha = \text{mod} \left( \sum_{\beta} h_{\alpha \beta}^{-1} x_{\beta}^a \right),
\]

where \( x_{\alpha}^a \) is \( \alpha \)-component of cartesian position vector of atom \( a \) in the \( \mathbf{L} = (l_1, l_2, l_3) \) unit cell of the solid. It follows from eq. 2 that the position derivatives of potential energy in the DFT+D approach are:

\[
\frac{\partial E_{\text{DFT+D}}}{\partial s_{\mu}^\alpha} = \frac{\partial E_{\text{KS-DFT}}}{\partial s_{\mu}^\alpha} + \frac{\partial E_{\text{disp}}}{\partial s_{\mu}^\alpha},
\]

where the term \( \frac{\partial E_{\text{KS-DFT}}}{\partial s_{\mu}^\alpha} \) is computed using the Hellmann-Feynman theorem and \( \frac{\partial E_{\text{disp}}}{\partial s_{\mu}^\alpha} \) is the contribution from Grimme’s potential:

\[
\frac{\partial E_{\text{disp}}}{\partial s_{\mu}^\alpha} = \frac{N_{\text{at}}}{2} \sum_{j=1}^{N_{\text{at}}} \sum_{L'} \partial E_{\text{disp}} \left( \frac{6}{|r_{\mu}^i - r_{\mu}^j|^6} - \frac{d}{R_{ij}} e^{-d(|r_{\mu}^i - r_{\mu}^j|/R_{ij}-1)} f(|r_{\mu}^i - r_{\mu}^j|) \right) \times C_{ij}^6 \frac{|r_{\mu}^i - r_{\mu}^j|^6}{|r_{\mu}^i - r_{\mu}^j|^6} \frac{\partial |r_{\mu}^i - r_{\mu}^j|^6}{\partial s_{\mu}^\alpha}.
\]

The lattice-vector derivatives of potential energy are computed using:

\[
\frac{\partial E_{\text{DFT+D}}}{\partial h_{\alpha \beta}} = -\Omega \sum_{\gamma} \sigma_{\alpha \gamma}^{\text{DFT+D}} (h_{\gamma \beta})^{-1},
\]

Here \( \Omega \) is volume of the unit cell and \( \sigma_{\alpha \gamma}^{\text{DFT+D}} \) is stress tensor that can be expressed as a sum of \( \sigma_{\alpha \gamma}^{\text{DFT}} \) computed at ab-initio level and a correction due to the force field \( \sigma_{\alpha \gamma}^{\text{D}} \). The latter term is computed as:

\[
\sigma_{\mu, \nu}^{\text{D}} = -\frac{1}{2\Omega} \sum_{i=1}^{N} \sum_{j=1}^{N} \sum_{L'} \partial E_{\text{disp}} \left( x_{\mu}^{i,0} \partial |r_{\mu}^i - r_{\mu}^j|^6 \right) \frac{\partial |r_{\mu}^i - r_{\mu}^j|^6}{\partial x_{\mu}^{i,0}}.
\]

**D. Structural optimizations and bulk modulus calculations**

Atomic positions and lattice volume and geometry have been optimized at the same time using the conjugate gradient method [30]. Bulk modulus has been determined by fitting
energies from series of constant volume optimizations (i.e. all degrees of freedom except volume have been optimized) to Murnaghan equation of states:

\[ E(V) = E_0 + \frac{B_0 V}{B'_0} \left( \frac{(V_0/V)^{B'_0}}{B'_0 - 1} + 1 \right) - \frac{B_0 V_0}{B'_0 - 1}. \]  

(11)

where \( B_0 \) is bulk modulus, \( B'_0 \) is the bulk modulus pressure derivative, \( E_0 \) is energy, and \( V_0 \) is volume of ground state. In principle, the optimal geometry and lattice parameters determined using full structural optimization should be the same as that obtained by \( E-V \) fitting. For most of systems discussed in this work this was indeed the case. In some cases, however, PBE predicts too weak interactions between individual entities (molecules or layers) which results in abnormally flat potential energy surface near minimum. In order to achieve reasonable convergence by automatic full structural optimizations, extremely tight relaxation criteria would be required, otherwise the minimizer may easily get stuck in an incorrect structure.

A further difficulty is related to the Pulay stress [31], which can strongly bias automatized optimizations with volume relaxation. This effect is related to the fact that during an optimization using the same set of plane waves, the quality of the basis set changes with volume and cell-shape variations, unless an absolute convergence has been attained in the size of the plane wave basis set. This can be achieved only with very large energy cutoff, at least 30 \% higher than the recommended value, but often one has to use even higher values. An alternative, less expensive way to avoid the artifacts related to the Pulay stress is to perform a series of fixed-volume optimizations and locate the minimal volume by fitting the energy-volume curve. This \( E-V \) fitting yields, in general, more reliable estimates of the optimal structures and energies. Hence in problematic cases (i.e. molecular crystals, graphite, and cellulose) we discuss structures obtained from an \( E-V \) fitting.

As a consequence of stronger dispersion interactions, the potential energy profiles are much deeper in PBE+D2 method and full PBE+D2 optimizations yield reliable results. To illustrate this behavior, the PBE and PBE+D2 energy profiles for graphite are shown in Fig. 1. In the case of PBE+D2 approach, the volume of ground-state obtained using the full lattice optimization (34.2 Å\(^3\)) is very close to the value obtained from \( E-V \) fitting (33.9 Å\(^3\)). On the other hand, the volume of structure obtained by full optimization of graphite using the PBE functional (43.2 Å\(^3\)) is too low compared to the ground-state volume from the \( E-V \) fitting (46.6 Å\(^3\)). It should be emphasized, however, that the energy difference
between these two structures is only $\sim 2$ meV per a unit cell.

E. Cohesive energy

The cohesive energies ($\Delta E_{\text{coh}}$) for some systems have been calculated using

$$\Delta E_{\text{coh}} = \frac{E_{\text{bulk}}}{N_{\text{unit}}} - E_{\text{unit}},$$  \hspace{1cm} (12)

where $E_{\text{bulk}}$ and $E_{\text{unit}}$ are total energies of bulk and of a single chemical entity (atom or molecule) in vacuum, respectively, and $N_{\text{unit}}$ is number of entities in the simulation cell. In calculations of $E_{\text{unit}}$, sufficiently large simulation cells were used in order to reduce interactions between atom or molecule and its repeated images. For the same reason, the cutoff radius for the force field was reduced in the case of PBE+D2 calculations.

III. STRUCTURAL OPTIMIZATION OF SELECTED SYSTEMS

A. Noble gas solids

Noble gases - neon, argon, krypton, and xenon crystallize in the face centered cubic (fcc) structures that are held together almost exclusively by van der Waals interactions. In our calculations, k-point grid of $8 \times 8 \times 8$ and a plane wave cutoff of 1000 eV have been used. The lattice parameters, bulk moduli, and cohesive energies computed with the PBE and PBE+D2 are presented together with available experimental data [32–39]), and results from other computational studies [40, 41] in Tab. II.

Although the PBE functional binds the noble gas atoms together to form a crystal, the attractive forces are much too weak and the equilibrium lattice parameters are too large compared with experiment. Correspondingly, the cohesive energies are too low and increase only slightly along the series. Also the shape of the energy-volume curves is too flat and therefore the computed bulk moduli are strongly underestimated. The only exception is the neon crystal for which the PBE performs rather well and all computed quantities are in good agreement with experiment. Exactly opposite holds for the PBE+D2 results where, except for neon, agreement with experiment is improved for all computed parameters. In the case of Ne, PBE predicted already reasonable values and therefore adding further interactions...
(Grimme’s force field) actually worsens results.

Ortmann et al. [40] used similar semi-empirical computational scheme to compute lattice constants and bulk moduli for Ne and Ar, see Tab. II. While slightly better agreement with experiment has been achieved for Ne, results for Ar are barely better than GGA results without any correction. Lattice constants and cohesive energies computed using the adiabatic connection fluctuation-dissipation theorem (ACDFT) within random phase approximation (RPA) are reported in Ref. [41], and excellent agreement with experiment has been achieved.

B. Molecular crystals

1. α-nitrogen

The α phase of nitrogen occurs in a limited area of the $p - T$ diagram, bounded roughly by pressures of 3500 to 4500 atm and temperatures 35 to 45 K [42]. The α-nitrogen forms simple cubic crystals with lattice parameter $a = 5.694$ Å [42] in which the N$_2$ molecules are held together by weak interactions, the experimentally measured heat of sublimation is 7.6 kJ/mol [43]. The measured length of N≡N bonds in the crystal is 1.066 Å [42].

The calculations have been performed with plane wave cutoff of 1000 eV and $8 \times 8 \times 8$ Monkhorst-Pack grid of k-points. As shown in Tab. III, PBE underestimates the strength of interactions between the N$_2$ molecules ($\Delta E_{coh} = 2.6$ kJ/mol) and hence the lattice constant is strongly overestimated ($a = 6.19$ Å). In contrast, the the N$_2 \cdots$N$_2$ interactions are strengthened in PBE+D2 method and the computed values for cohesive energy (8.5 kJ/mol) and lattice parameter (5.65 Å) are in very good agreement with experiment. The computed length of N≡N bonds in the crystal is 1.112 Å, the same value as obtained using the PBE functional.

2. Benzene

Benzene is another example of molecular crystal in which molecules are held together by weak intermolecular forces, dominated by London dispersion (stacking) and quadrupole-quadrupole multipolar electrostatic interactions. Individual molecules are arranged such as to form puckered layers parallel to the (001) plane. Experimental lattice parameters for the
orthorhombic cell with space group Pbca are \( a = 7.292 \, \text{Å}, b = 9.471 \, \text{Å}, c = 6.742 \, \text{Å} \) [44]. In our calculations the plane wave cutoff was set to 800 eV and a \( 2 \times 2 \times 2 \) Monkhorst-Pack grid of k-points was used. The calculated and experimental results are compared in Tab. IV.

Although the six-fold rotational symmetry of the benzene molecule is broken in the crystal, lengths of all C−C bonds remain close to value of 1.378 Å [44] and the C−C−C angles are all in the interval between 119.5° to 120.8°. The PBE and PBE+D2 methods predict very similar intramolecular parameters for benzene: \( r_{\text{C−C}} = 1.399 \, \text{Å} \) (PBE), and 1.398 Å (PBE+D2) and the C−C−C angles range between 120.0 to 120.2° (PBE), and 119.8 to 120.4° (PBE+D2).

While computed intramolecular parameters for benzene in crystal agree well with experiment, the geometry of the unit cell predicted by PBE differs significantly. The computed lengths of lattice vectors are \( a = 8.06 \, \text{Å}, b = 10.15 \, \text{Å}, \) and \( c = 7.53 \, \text{Å} \). The energy versus volume curve computed with PBE functional is rather flat near the minimum and the computed bulk modulus is only 1 GPa, much too low compared to experimental value of 8 GPa [45]. All these results show that the weak physical interactions between individual benzene molecules are strongly underestimated by the PBE functional. Not surprisingly, computed cohesive energy of 9.7 kJ/mol is by far too low compared to experimentally measured heat of sublimation of 43-47 kJ/mol [46]. Inclusion of Grimme’s potential improves agreement with experiment for all computed quantities: \( a = 7.09 \, \text{Å}, b = 9.07 \, \text{Å}, c = 6.54 \, \text{Å}, B_0 = 10 \, \text{GPa}, \) and \( \Delta E_{\text{coh}} = 55.7 \, \text{kJ/mol} \).

Our results can be compared with other theoretical studies. Civalleri et al. [15] have shown that B3LYP functional strongly overestimates lattice parameters \( (a = 8.592, b = 8.674, c = 8.588) \) whereas B3LYP+D with modified Grimme’s correction improves agreement with experiment \( (a = 7.343 \, \text{Å}, b = 9.193 \, \text{Å}, c = 6.578 \, \text{Å}) \). Exact exchange random phase approximation (EXX/RPA) calculations have been conducted by Lu et al. [19]. Excellent agreement with experiment has been reported for ground-state volume, bulk modulus \( (B_0 = 7.5 \, \text{GPa}) \), and cohesive energy \( (\Delta E_{\text{coh}} = 47 \, \text{kJ/mol}) \). As the energy gradients are not available in the EXX/RPA method, the shape of the cell has not been optimized and the values of lattice vectors are not reported.
3. Cytosine

Cytosine is one of four nucleobases found in deoxyribonucleic acid. Cytosine crystallises in orthorhombic lattice with space group $P2_12_12_1$, the experimental cell parameters are $a = 13.041 \text{ Å}$, $b = 9.494 \text{ Å}$, $c = 3.815 \text{ Å}$ [47]; see Fig. 2. The individual molecules in the crystal interact mainly via hydrogen bonds, the measured heat of sublimation is 155.0 kJ/mol [48].

The geometry optimization of cytosine has been performed with plane wave cutoff of 800 eV and grid of $1 \times 1 \times 3$ k-points. The computational results and experimental data are compiled in Tab. V. The PBE functional fails in describing the geometry of crystalline cytosine. Especially the parameter $c = 5.32 \text{ Å}$ is significantly overestimated compared to the experimental value. The intramolecular bond lengths, however, are rather close to experimentally measured values, see Tab. VI and Fig. 3. Computed cohesive energy is 105.9 kJ/mol, which is significantly lower value than that predicted by experiment.

The PBE+D2 method predicts the structure that is in very good agreement with experiment: $a = 12.93 \text{ Å}$ $b = 9.46 \text{ Å}$ $c = 3.64 \text{ Å}$. Although both PBE and PBE+D2 predict distinctly different lattice geometries, the computed intramolecular bond lengths are very similar, see Tab. VI. The calculated cohesive energy of 162.5 kJ/mol is comparable with the experimentally measured heat of sublimation of 155.0 kJ/mol [48].

C. Layered materials

1. Graphite

Graphite is a layered allotrope of carbon with hexagonal crystal structure. The experimentally measured [49] lattice parameters are $a = 2.462$ and $c = 6.707 \text{ Å}$. The measured cohesive energy of graphite is $-7.371 \text{ eV/atom}$ [50]. Structural optimizations of graphite have been performed with hexagonal cell with four carbon atoms. The plane-wave cutoff was set to 1000 eV and a $16 \times 16 \times 8$ mesh was used for the Brillouin zone sampling. Computed and experimental lattice parameters and bulk moduli are compared in Tab. VII. It is well known that the PBE functional fails in predicting the structure of graphite, in particular, it underestimates strongly the weak dispersion interactions that are dominant in the stacking direction and therefore the corresponding lattice parameter is strongly overestimated, $c = 8.84 \text{ Å}$. The lattice vector $a$ is parallel with sheets of covalently bonded carbon atoms.
This type of interaction is described well by the PBE functional and the computed value $a = 2.47 \, \text{Å}$ is in very good agreement with experiment. As a consequence of too weak interlayer interactions, the computed bulk modulus $B_0 = 1.4 \, \text{GPa}$ is too low compared to experimental values 34-42 GPa [49, 51]. The computed cohesive energy is $-7.989 \, \text{eV/atom}$, which is too low compared to experiment [50].

Adding the dispersion interaction correction leads to substantial improvement in predicted cell geometry. The parameter $c$ decreases to 6.45 Å but the other lattice parameter is barely affected, $a = 2.46 \, \text{Å}$. Due to added attractive interactions, the cohesive energy computed with PBE+D2 approach ($-8.099 \, \text{eV/atom}$) is even slightly lower compared to the PBE result. Bulk modulus computed with PBE+D2 functional is 37.8 GPa which is in excellent agreement with experiments [49, 51]. Very similar results have been reported in other theoretical studies in which PBE+D2 method has been used: Barone et al. [17] computed values $a = 2.466$, $c = 6.430 \, \text{Å}$, and $B_0 = 46.5 \, \text{GPa}$, Kerber et al. [16] obtained $c = 6.400 \, \text{Å}$ (parameter $a$ was fixed at experimental value). Similar results ($a = 2.455$, $c = 6.690 \, \text{Å}$, and $B_0 = 41.7 \, \text{GPa}$) have been reported by Ortmann et al. [40] who used semiempirical scheme with different parametrization (GGA+vdW). Rydberg et al. [52] used their non-local van der Waals density functional (vdW-DF) [53] to determine crystal structure and bulk modulus of graphite. The computed values ($a = 2.47 \, \text{Å}$, $c = 7.52 \, \text{Å}$, and $B_0 = 12 \, \text{GPa}$) are qualitatively worse than those from the PBE+D2 scheme.

2. h-boron nitride

Hexagonal form of boron nitride (h-BN) has a layered structure similar to graphite. Within each layer, each boron is covalently bound with three nitrogen atoms and vice versa. The BN layers, held together by weak van der Waals interactions, are stacked in such a way that boron atoms are located directly above or below the nitrogen atoms. In the experimentally determined crystal structure [54], the in-plane lattice parameter is $a = 2.503 \, \text{Å}$ and the length of lattice vector parallel with the stacking direction is $c = 6.661 \, \text{Å}$.

The calculations have been performed with k-points grid of $16 \times 16 \times 8$, and a plane-wave cut-off of 1500 eV. Within the PBE functional, the interaction between individual BN layers is negligibly small and hence we could not identify a corresponding ground state. This is considerably improved when using the dispersion correction: the layers are bound
together and the length of the lattice vector $c$ is shortened to 6.17 Å. Similar to PBE+D2 optimization of graphite, this value is shorter than that predicted by experiment indicating that Grimme’s force field tends to over-correct van der Waals interactions. The in-plane lattice parameter, governed mainly by strong covalent interactions, is reproduced with a good accuracy, $a = 2.51$ Å. The bulk modulus computed using PBE+D2 is 56 GPa which is too large compared to experimental value of 37 GPa [55]. As PBE functional predicts basically no binding between different layers; we were not able to compute $B_0$ at this level of theory.

It is instructive to compare our PBE+D2 results with the ones obtained by other methods published in the literature. Using semi-empirical GGA+vdW method, Ortmann et al. [40] determined the lattice parameters $a = 2.496$ Å, $c = 6.550$ Å, and bulk modulus $B_0 = 43$ GPa. Rydberg et al. [52], optimized the crystal structure of $h$-BN using the van der Waals density functional (vdW-DF) [53]. While the reported value of the lattice parameter $a = 2.51$ Å, is in good agreement with experiment, the equilibrium interlayer distance is significantly overestimated, $c = 7.26$ Å. Using the adiabatic-connection fluctuation-dissipation theorem (ACFDT) [56-58] in the random phase approximation, Marini et al. [59] have obtained a value of $c = 6.61$ Å that is in excellent agreement with experiment.

3. Potassium graphite

In potassium graphite ($C_8$K), one carbon sheet is alternating with one layer of potassium (see Fig. 4), the bonds between potassium and carbon atoms have ionic character. While the carbon layers are stacked in an AA type, the K atoms occupy the sites above the hollows of every fourth carbon hexagon. The experimental lattice parameters for hexagonal cell are $a = 4.960$ and $c = 21.400$ Å. In our simulations, we have used a cell with 32 carbon and 4 potassium atoms. The calculations have been carried out with grid of $4 \times 4 \times 2$ k-points and a plane-wave cut-off of 1500 eV. Results are collected in Tab. VII.

As the character of interactions along the stacking direction is ionic, unlike for graphite, PBE yields results that are in reasonable agreement with experiment [60, 61], the computed lattice parameters are $a = 4.98$ Å and $c = 21.48$ Å. The van der Waals interactions appear to play only minor role in the stabilization of the $C_8$K structure, hence PBE+D2 predicts qualitatively similar results: $a = 4.96$ Å and $c = 21.12$ Å.
An accurate experimental value of bulk modulus for potassium graphite is, to our best knowledge, not available. For laterally rigid materials, however, the elastic constant $C_{33}$ can serve as a good approximation for this quantity. Using $C_{33}=47$ GPa measured by Wada et al [62], it follows that PBE slightly underestimates ($B_0 = 40$ GPa) while PBE+D2 overestimates ($B_0 = 64$ GPa) bulk modulus for potassium graphite.

This system has been investigated also with the vdW-DF method [63]. As in the case of graphite and boron nitride, the vdW-DF method yields qualitatively worse results compared to PBE+D2. In particular, the length of lattice vector parallel with the stacking direction is significantly overestimated, $c = 22.12$ Å while bulk modulus $B_0 = 26$ GPa is too low compared to experiment.

4. $\beta$-MoS$_2$ and NbSe$_2$

Molybdenum disulfide ($\beta$-MoS$_2$) crystallizes in a hexagonal structure consisting of S–Mo–S layers, each unit cell contains two such layers. The individual layers are bound to each other by weak van der Waals forces, see Fig. 5. In the crystal, the molybdenum atoms of one layer are directly above the sulfur atoms of the other layer and vice versa. Theoretical study of two dimensional MoS$_2$ (and NbSe$_2$) has been presented recently [64], but the effect of the stacking was ignored in order to focus on the two-dimensional properties. Experimental study of MoS$_2$ was reported by Bronsema et al. [65], the corresponding lattice parameters and volume are reported in Tab. VIII. The structural properties of MoS$_2$ were calculated using a plane-wave cutoff of 1500 eV and a k-point mesh of $8 \times 8 \times 8$. As found before [66], PBE is strongly overestimating the lattice parameter parallel to the stacking direction. Also the atomic shift of sulfur with respect to molybdenum atoms $z$ (see Fig. 5) is strongly overestimated. The situation is greatly improved when using PBE+D2: the deviation of computed lattice vector $c$ from the experimental value has been reduced to 0.13 Å and the $z$ parameter of 0.125 is close to experimental value of 0.121. The estimated in-plane lattice parameter is similar to the one found with the PBE method ($a = 3.19$ Å). The PBE+D2 provides also much better estimates of bulk modulus, the computed values are 2 GPa (PBE), 39 GPa (PBE+D2), while the experimental value [67] is 53 GPa. The PBE+D2 approach, however, seems to overestimate the cohesive energy: the computed value is $-5.37$ while the experimental cohesive energy is $-5.18$ eV/atom [68].
functional ($-5.12 \text{ eV/atom}$), on the other hand is in excellent agreement with experiment. Similar value ($\Delta E_{\text{coh}} = -5.11 \text{ eV/atom}$) has been obtained by Raybaud et al. [68] using the PW91 functional.

The vdW-DF calculations of the MoS$_2$ structure have been performed by Rydberg et al. [52]. The reported values for lattice parameters and for bulk modulus are $a = 3.23$ Å and $c = 12.6$ Å, and $B_0 = 39$ GPa, respectively.

The structure of NbSe$_2$ is similar to the MoS$_2$: every niobium layer is intercalated between two selenium layers. NbSe$_2$ is particularly interesting in solid state science, due to its superconducting properties and the presence of charge density waves. The computed and experimental [69] lattice parameters are compiled in Tab. VIII. In the simulations, a plane wave cutoff of 1500 eV and a k-point mesh of $12 \times 12 \times 8$ have been used. As in the case of MoS$_2$ we find that dispersion correction is necessary to obtain a reasonable agreement of theoretical structures with experimental data. The bulk modulus values obtained by PBE and PBE+D2 are completely different: 5.7 GPa (PBE), and 42 GPa (PBE+D2), respectively. The experimental value for bulk modulus of NbSe$_2$ is not available but it can be expected to be similar to that for MoS$_2$.

5. Vanadium pentoxide

Vanadium pentoxide ($V_2O_5$) is another layered material with weak interactions between the layers. It crystallizes in an orthorhombic lattice, with two formula units per cell, and four crystallographically inequivalent atoms (one vanadium and three oxygens). The experimental determination of the structure was performed by Enjalbert and Galy [70]. The reported lattice parameters are $a = 11.51$ Å, $b = 3.56$ Å, $c = 4.37$ Å. In our simulations, a plane-wave cutoff of 1500 eV and a k-points mesh of $4 \times 8 \times 8$ were used. Results are compiled in Tab. IX. The PBE functional reproduces the in-plane lattice parameters rather well ($a = 11.54$ Å and $b = 3.57$ Å), while it strongly overestimates the parameter $c$ (4.83 Å). Qualitatively similar results have been reported in previous DFT studies [71–75]. It should be noted, however, that the actual values of lattice parameters depend strongly on the particular computational setting giving rise to significant uncertainty in published computational results. For instance, using the same simulation software (VASP) and the same DFT functional (PW91), Reeswinkel et al. [75] reported value of parameter $c = 4.40$ Å (plane
wave cutoff 500 eV) Goclon et al. [74] found 4.66 Å (600 eV) while Ganduglia-Pirovano et al. [72] obtained $c = 4.84$ Å with a cutoff of 800 eV. This latter result is in good agreement with the structure found in the present PBE calculations.

As expected, the PBE+D2 approach strengthens binding between the layers leading to contraction of the lattice parameter $c$ (4.47 Å), while it predicts slightly worse values for the lattice parameters $a$ and $b$. The stronger binding between the layers is also reflected into the shortest distance between the vanadium atoms and the oxygen pointing out of the layers (parameter $d$, see Fig. 6 and Tab. X): the experimental value is 2.79 Å, PBE+D2 yields a value of 2.86 Å, whereas PBE predicts distance of 3.23 Å. The values of bond lengths between vanadium and three different oxygen atoms obtained using PBE and PBE+D2 are similar and reasonably close to the experimental values, see Tab. X. The computed bulk moduli can be compared it with the experimental value of 50 GPa[76]. Although the PBE+D2 estimate is qualitatively better (33 GPa) than the PBE result (10 GPa), it is still significantly lower than the measured bulk modulus.

The structure of vanadium pentoxide has been recently investigated using the PBE+D2 method by Kerber et al. [16]. The reported interlayer equilibrium distance of 4.50 Å is comparable with our PBE+D2 result of 4.47 Å. The small difference is probably due to the fact that the lattice parameters $a$ and $b$ were fixed at experimental values in the calculations of Kerber et al. [16], whereas in our simulations these parameters have been relaxed.

D. Crystal structures with isolated atomic or molecular chains

1. Selenium and tellurium

The structure of $\gamma$-phases of selenium and tellurium consist of covalently bonded helical chains, held together by vdW forces. The atomic parameter $u$ is related by $u = q/a$ to the radius $q$ of the helices [77]. Some previous LDA and GGA calculations [78] failed to reproduce the experimental structural data satisfactorily, presumably because of the absence of a correct modeling of dispersion forces. The calculations presented in this sections have been performed with a plane-wave cut-off of 1500 eV and a k-point mesh of $6 \times 6 \times 6$. The experimental and computational results are compiled in Tab. XI. For selenium, PBE predicts too large volume and too low bulk modulus compared with experiment [77]. In addition
to lattice geometry, important internal parameters have been analyzed. The experimental and theoretical values for the shortest Se–Se distance between atoms in the same chain \((d_1)\), the Se–Se–Se bonding angle \((\theta)\), and the shortest Se-Se distance between atoms in different chains \((d_2)\) (see Fig. 7) are compiled in Tab. XII. Clearly, the incorrect description of dispersion forces is most significantly reflected into value of parameter \(d_2\) (3.57 Å with PBE, while the experimentally value is 3.44 Å). This structural parameter is improved when using the PBE+D2 method. Compared to the PBE result, \(d_2\) is shortened by 0.2 Å which leads to the reduction of the cell volume. The intra-chain parameters \((d_1\) and \(\theta)\), on the other hand, are described correctly by both PBE and PBE+D2 method. The value of internal structural parameter \(u\) is underestimated by PBE and overestimated by PBE+D2 by about the same amount. The bulk modulus computed by PBE+D2 (8 GPa) is closer to the experimental value of 14.9 GPa [77] than that predicted by PBE (4 GPa), although the agreement with experiment is not perfect.

In the case of tellurium, simple PBE calculations provide already a fairly good description of structure. In particular, the inter-chain distance is correct and the volume of the cell is only slightly overestimated. The PBE+D2 reduces \(d_2\) and the volume of the cell, but the correction is somewhat exaggerated. The internal structural parameter \(u\) computed with PBE (0.270) is closer to experimental value (0.263) than that obtained with PBE+D2 approach (0.277). In summary, the performance of PBE+D2 method in prediction of structure of tellurium is slightly worse than that for PBE. The same holds true also for the bulk modulus: the PBE result of 18 GPa is closer to the experimental value of 19.4 GPa [77] than the bulk modulus computed with PBE+D2 method (23 GPa).

2. Cellulose Iβ

Cellulose is a polymer in which the D-glucose units are linked via \(\beta(1 \rightarrow 4)\)-glycosidic bonds. Phase Iβ – one of many crystalline forms of natural cellulose – crystallises in monoclinic structure \(a = 7.784, b = 8.201, c = 10.380\) Å, and \(\gamma = 96.6^\circ\) [79]. The D-glucose polymers are stacked in such a way that the dominant interactions along three lattice vectors of monoclinic cell (see Fig. 8) are of different nature: weak dispersion interactions along vector \(a\), hydrogen bonds along \(b\), and strong covalent interactions along lattice vector \(c\).

In our simulations, the plane wave cutoff was set to 800 eV and \(2 \times 2 \times 1\) k-point mesh
was used for a Brillouin zone sampling. The computational results are compared with the experimental data \cite{79} in Tab. XIII. The PBE simulation of cellulose I\(\beta\) illustrates ability of the functional to describe different types of interactions. While the lengths of lattice vectors \(b = 8.23\) and \(c = 10.46\,\text{Å}\) that are governed mainly by hydrogen and covalent bonds, respectively, agree reasonably well with the experimental data, the length of vector \(a\) is significantly overestimated, \(a = 8.70\,\text{Å}\). Also the shape of the cell is significantly deformed as obvious by comparing computed and experimental values of parameters \(\gamma\), \(b/a\), and \(c/a\). The PBE+D2 functional predicts structure that agrees rather well with experiment: \(a = 7.65\,\text{Å}, b = 8.14\,\text{Å}, c = 10.39\,\text{Å}\), and \(\gamma = 96.8^\circ\).

In ref. \cite{79}, crystallographic data including atomic positions are available hence we have opportunity to compare the theoretical intramolecular geometry with experiment. As the number of internal coordinates such as bond lengths, angles and torsions characterizing the structure of cellulose I\(\beta\) is rather large, we do not report all the values here. Instead, in order to facilitate the comparison, we measure the computational error by means of root mean square (RMS) of deviations from experimental values. The RMS for the geometry optimized using the PBE functional is 0.004 Å for bond lengths, 5.7° for angles and 22.6° for torsions. As in the case of lattice parameters, the agreement with experiment improves when using the PBE+D2 functional: the RMS is reduced to 0.002 Å, 3.9°, and 10.9°, for bond lengths, angles and torsions, respectively. It is remarkable that the error bars are even smaller if one ignores the coordinates containing H atoms. While in the PBE calculations the mean deviations for heavy atoms coordinates are 0.004 Å, 4.1°, and 12.4°, from the PBE+D2 calculations one obtains 0.003 Å, 2.9°, and 6.7°. This better agreement with raw experimental data is certainly related to experimental uncertainties and systematic errors in the H-atom positions obtained by X-ray diffraction.

E. Covalent and ionic crystals

In previous sections we focused mainly on systems in which the dispersion interactions play important role in stabilizing their structures. However, the PBE+D2 approach would be of little use if it would fail to describe the structure of systems dominated by other type of interactions such as covalent and ionic crystals. In this section, we test the performance of PBE+D2 in structural optimization of diamond, silicon, sodium chloride as well as of the
mineral chabazite for which standard PBE yields already very reasonable results.

1. **Diamond, silicon, and sodium chloride**

All simulations have been performed with plane-wave cutoff of 500 eV and a k-point mesh of $16 \times 16 \times 16$. The computed equilibrium lattice parameters and bulk moduli for diamond, silicon, and sodium chloride are compared with experimental data in Tab. XIV. For all three systems, PBE overestimates the equilibrium lattice constants. Although van der Waals interactions are not dominant in these systems, PBE+D2 tends to improve agreement with experiment. The situation is slightly different for the bulk moduli: compared to the PBE results, PBE+D2 improves agreement with experiment for diamond and silicon but it performs slightly worse (although still reasonably well) for NaCl. In summary, the performance of PBE and PBE+D2 is comparable for covalent and ionic solids.

For diamond, the cohesive energy has been determined. The computed values are $-7.855$ (PBE) and $-8.069$ (PBE+D2) eV/atom, both values being too low compared to measured cohesive energy of $-7.346$ eV/atom [50]. It is interesting, however, to compare difference in $\Delta E_{coh}$ between diamond and graphite. Based on experimental data [50], the cohesive energy for diamond is $\sim 0.02$ eV/atom higher compared to graphite. The PBE method predicts difference of 0.13 eV/atom while the PBE+D2 result of 0.03 eV/atom is very close to the experimental value.

2. **SiO$_2$ chabazite**

Chabazite is microporous aluminosilicate mineral in which every Si and Al atom is coordinated by four O atoms. In this study we consider purely siliceous version of this mineral. In order to reduce computational costs, primitive monoclinic, instead of crystallographic hexagonal cell [80] has been used in simulations. The corresponding experimental lattice parameters are $a = 9.291$ Å, and $\alpha = 93.9^\circ$ [81]. The simulation cell contains 12 silicon and 24 oxygen atoms. The dominant interaction in chabazite is a covalent bonding, van der Waals interactions are not expected to play important role in stabilizing of the chabazite structure. In the simulations, the plane wave cutoff was set to 800 eV and $2 \times 2 \times 2$ k-point mesh was used for a Brillouin zone sampling. As obvious from data collected in Tab. XV, both func-
tionals overestimate parameter $a$ and the cell volume slightly, but more importantly, both functionals predict very similar structures. Also the agreement in internal parameters is almost perfect, the values of RMS of deviation in internal parameters computed using PBE and PBE+D2 are 0.002 Å, 0.8° and 2.0° for Si–O bond lengths, Si–O–Si and O–Si–O bonding angles, and O–Si–O–Si torsions, respectively. The computed bulk moduli are 68.2 and 71.5 GPa using PBE and PBE+D2, respectively. These values are in reasonable agreement with experimental value of 62 GPa reported by Leardini et al. [82].

IV. CONCLUSIONS

In this work, we have systematically tested performance of semiempirical PBE+D2 approach on different systems including noble gas solids, molecular crystals, crystals with isolated atomic and molecular chains, layered materials, and covalent and ionic crystals. In general, the dispersion correction leads to more realistic predictions of lattice parameters and bulk moduli for systems for which the standard PBE functional fails.

The fact that PBE+D2 performs very well also for systems in which the van der Waals interactions are not supposed to play an important role and which are reasonably well described by PBE is of eminent importance as it indicates that PBE+D2 can be used as a tool for structural optimizations for arbitrary system regardless of the nature of dominant interactions. Moreover, applications of PBE+D2 can be extended to cases in which different subsystems are governed by different type of interactions. Example for such a case is alkane adsorption in zeolites: the interactions within an alkane and zeolite alone are mainly of covalent character but the mutual interaction is dominated by van der Waals forces. Our preliminary results [83] indicate that the PBE+D2 method improves significantly predicted adsorption energies of short alkanes at acidic zeolites.

Although, as we have shown, PBE+D2 leads to improvement of structural predictions for extended systems, the agreement with experiment is not perfect. In almost all systems studied in this work, we have observed systematic overestimation of vdW interactions (as indicated by somewhat underestimated lattice parameters). This is not surprising as the Grimme potential was originally not designed for periodic systems. In the future, performance of PBE+D2 method can be improved by fine tuning of the force field parameters, in particular dispersion coefficients $C_6$ and global scaling parameter $s_6$, see eq. 2.
Finally, performance of PBE+D2 can be compared with other methods currently available to deal with vdW interactions. A non-local density functional (vdW-DF) developed to account for van der Waals interactions [53] exists in a self-consistent version [84, 85] adapted for analytical force calculations. It has been applied to structural optimizations of layered materials involving graphite [52, 63], boron nitride [52], MoS$_2$ [52], and potassium graphite [63]. According to published results, this level of theory tends to systematically overestimate lengths of lattice vectors parallel with stacking directions. For all above mentioned systems, the PBE+D2 method yields qualitatively better predictions. Performance of RPA-ACDFT method on solids including noble gas crystals [41], benzene [19], and boron nitride [59] has been studied. Excellent agreement between theoretical and experimental results has been reported. This level of theory is obviously superior to semiempirical PBE+D2, but unfortunately, energy gradients for RPA-ACDFT are currently not available making the full optimizations extremely impractical for even medium sized systems. The computationally inexpensive PBE+D2 method, on the other hand, represents a reasonable compromise between accuracy and computational costs and can extend range of applications of standard Kohn-Sham DFT calculations for extended systems and solids. The success of Grimme’s scheme as compared to the numerous attempts to parametrize a DFT+D flavor method is that it succeeds in matching the behavior of various specific functionals to the dispersion energy formula and thus avoiding most of the spurious effects that may arise in the intermediary region of interatomic distances, where both the functional and the dispersion correction have non-negligible contributions.

APPENDIX A: VASP KEYWORDS

Since the PBE+D2 approach is now available in the official release of the VASP package, we provide below the corresponding keywords (to be put in the INCAR file) which control this feature.

- **LVDW** = .false. or .true. (default is .false.). If set to .true., DFT+D2 method is invoked.

- **VDW_RADIUS** = cutoff radius in Å for the summation in Eq. 2 (default is 30 Å).
• **VDW** _SCALING_ = global scaling parameter $s_6$, see Eq. 2 (default is 0.75).

• **VDW** _D_ = parameter $d$ in the damping function defined in Eq. 3 (default is 20).

• **VDW** _C6_ = list of $C_6^i$ parameters in Jnm$^6$mol$^{-1}$. When this flag is used, the user must provide a $C_6^i$ for each species present in the system. The default values are the ones reported in the article of S. Grimme [10]. At the moment, only the $C_6^i$ from H (Z=1) to Xe (Z=54) are provided by default.

• **VDW** _R0_ = list of $R_i^j$ parameters in Å. When used, the list must contain $R_i^j$ for each species. The default values correspond to the ones reported in the original article describing this method [10], from H to Xe.

The total energy, corresponding to 2, is obtained by summing the standard total energy together with the one reported as the “Estimated vdW energy” in the **OUTCAR** file.


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[64] Lebègue, S. and Eriksson, O., Mar, (2009), 79(11), 115409.


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TABLE I: Parameters for Grimme’s PBE+D2 force field used in this study (after Ref. [10]).

<table>
<thead>
<tr>
<th>Element</th>
<th>( C_0 )</th>
<th>( R^i )</th>
<th>Element</th>
<th>( C_0 )</th>
<th>( R^i )</th>
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<td>Cl</td>
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<td>1.639</td>
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<tr>
<td>B</td>
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<td>1.485</td>
<td>Ar</td>
<td>4.61</td>
<td>1.595</td>
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<td>C</td>
<td>1.75</td>
<td>1.452</td>
<td>K</td>
<td>10.80</td>
<td>1.485</td>
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<td>N</td>
<td>1.23</td>
<td>1.397</td>
<td>V</td>
<td>10.80</td>
<td>1.562</td>
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<td>O</td>
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<td>Se</td>
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<td>Na</td>
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<td>1.892</td>
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<td></td>
<td></td>
<td>Xe</td>
<td>29.99</td>
<td>1.881</td>
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TABLE II: Computed equilibrium lattice constants, bulk moduli, and cohesive energies for Ne, Ar, Kr, and Xe fcc crystals, compared with results from other theoretical studies and with experimental data.

<table>
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<tr>
<th>Compound</th>
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<th>$B_0$ (GPa)</th>
<th>$\Delta E_{coh}$ (meV/atom)</th>
</tr>
</thead>
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<tr>
<td>Ne</td>
<td>Expt</td>
<td>4.464 (Ref. [32])</td>
<td>1.1 (Ref. [32])</td>
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<td></td>
<td>PBE</td>
<td>4.56</td>
<td>1</td>
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<td></td>
<td>PBE+D2</td>
<td>4.23</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td>GGA+vdW (Ref. [40])</td>
<td>4.562</td>
<td>2.1</td>
</tr>
<tr>
<td></td>
<td>RPA (Ref. [41])</td>
<td>4.5</td>
<td>-17</td>
</tr>
<tr>
<td>Ar</td>
<td>Expt</td>
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<td>2.7 (Ref. [33])</td>
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<td>5.92</td>
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<td></td>
<td>PBE+D2</td>
<td>5.38</td>
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<td></td>
<td>GGA+vdW (Ref. [40])</td>
<td>6.002</td>
<td>0.9</td>
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<td></td>
<td>RPA (Ref. [41])</td>
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<td>$-83$</td>
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<tr>
<td>Kr</td>
<td>Expt</td>
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<td>3.6 (Ref. [36])</td>
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<td>PBE+D2</td>
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<td>4</td>
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<td></td>
<td>RPA (Ref. [41])</td>
<td>5.7</td>
<td>$-112$</td>
</tr>
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<td>Expt</td>
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<td>PBE</td>
<td>7.01</td>
<td>$&lt;1$</td>
</tr>
<tr>
<td></td>
<td>PBE+D2</td>
<td>6.06</td>
<td>6</td>
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TABLE III: Computed and experimental lattice parameter (a), length of bond between nitrogen atoms in the N$_2$ molecule in the crystal (r$_{N,N}$), bulk modulus ($B_0$), and cohesive energy ($\Delta E_{coh}$) for $\alpha$-nitrogen (cubic lattice).

<table>
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<tr>
<th>Method</th>
<th>a (Å)</th>
<th>r$_{N,N}$ (Å)</th>
<th>$B_0$ (GPa)</th>
<th>$\Delta E_{coh}$ (kJ/mol)</th>
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<tbody>
<tr>
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</tr>
<tr>
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<td>1.112</td>
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<td>$-$2.6</td>
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<td>PBE+D2</td>
<td>5.65</td>
<td>1.112</td>
<td>2</td>
<td>$-$8.5</td>
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TABLE IV: Computed and experimental volume, lattice parameters and bulk modulus for benzene (space group Pbca).

<table>
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<tr>
<th>Method</th>
<th>V (Å$^3$)</th>
<th>a (Å)</th>
<th>b (Å)</th>
<th>b/a</th>
<th>c (Å)</th>
<th>c/a</th>
<th>$B_0$ (GPa)</th>
<th>$\Delta E_{coh}$ (kJ/mol)</th>
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<td>Expt (Ref. [44])</td>
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<td>7.292</td>
<td>9.471</td>
<td>1.336</td>
<td>6.742</td>
<td>0.925</td>
<td>8 (Ref. [45])</td>
<td>$-$43-47 (Ref. [46])</td>
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<td>PBE</td>
<td>615.3</td>
<td>8.05</td>
<td>10.15</td>
<td>1.260</td>
<td>7.53</td>
<td>0.935</td>
<td>1</td>
<td>$-$9.7</td>
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<tr>
<td>PBE+D2</td>
<td>420.3</td>
<td>7.09</td>
<td>9.07</td>
<td>1.280</td>
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<tr>
<td>B3LYP (Ref. [15])</td>
<td>640.0</td>
<td>8.592</td>
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TABLE V: Computed and experimental volume, lattice parameters and bulk modulus for cytosine (orthorhombic lattice, space group P2$_1$2$_1$2$_1$).

<table>
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<tr>
<th>Method</th>
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<th>a (Å)</th>
<th>b (Å)</th>
<th>b/a</th>
<th>c (Å)</th>
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<tr>
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<td>$-$155.0 (Ref. [48])</td>
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<td>9.50</td>
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<td>0.434</td>
<td>4</td>
<td>$-$105.9</td>
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<td>0.732</td>
<td>3.64</td>
<td>0.282</td>
<td>14</td>
<td>$-$162.5</td>
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TABLE VI: Comparison of intramolecular bond lengths in crystalline cytosine determined experimentally [47] and theoretically. The atoms are numbered as in Fig. 3.

<table>
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<tr>
<th>Bond</th>
<th>Expt (Å)</th>
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<th>PBE+D2 (Å)</th>
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</thead>
<tbody>
<tr>
<td>N(1)-C(2)</td>
<td>1.374</td>
<td>1.393</td>
<td>1.389</td>
</tr>
<tr>
<td>C(2)-N(3)</td>
<td>1.364</td>
<td>1.359</td>
<td>1.358</td>
</tr>
<tr>
<td>N(3)-C(4)</td>
<td>1.337</td>
<td>1.352</td>
<td>1.348</td>
</tr>
<tr>
<td>C(4)-C(5)</td>
<td>1.424</td>
<td>1.432</td>
<td>1.429</td>
</tr>
<tr>
<td>C(5)-C(6)</td>
<td>1.342</td>
<td>1.363</td>
<td>1.362</td>
</tr>
<tr>
<td>C(6)-N(1)</td>
<td>1.357</td>
<td>1.356</td>
<td>1.355</td>
</tr>
<tr>
<td>C(2)-O(7)</td>
<td>1.234</td>
<td>1.265</td>
<td>1.265</td>
</tr>
<tr>
<td>C(4)-N(8)</td>
<td>1.330</td>
<td>1.340</td>
<td>1.339</td>
</tr>
</tbody>
</table>

TABLE VII: Computed and experimental volume, lattice parameters and bulk moduli for compounds with graphite-like structure.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Method</th>
<th>V (Å³)</th>
<th>a (Å)</th>
<th>c (Å)</th>
<th>c/a</th>
<th>B₀ (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Graphite</td>
<td>Expt</td>
<td>35.2</td>
<td>2.462 (Ref. [49])</td>
<td>6.707 (Ref. [49])</td>
<td>2.724</td>
<td>34-42 (Refs. [49, 51])</td>
</tr>
<tr>
<td></td>
<td>PBE</td>
<td>46.6</td>
<td>2.47</td>
<td>8.84</td>
<td>3.579</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>PBE+D2</td>
<td>33.9</td>
<td>2.46</td>
<td>6.45</td>
<td>2.622</td>
<td>38</td>
</tr>
<tr>
<td>h-BN</td>
<td>Expt</td>
<td>36.1</td>
<td>2.503 (Ref. [54])</td>
<td>6.661 (Ref. [54])</td>
<td>2.661</td>
<td>37 (Ref. [55])</td>
</tr>
<tr>
<td></td>
<td>PBE</td>
<td>no binding</td>
<td>no binding</td>
<td>no binding</td>
<td>no binding</td>
<td>no binding</td>
</tr>
<tr>
<td></td>
<td>PBE+D2</td>
<td>33.6</td>
<td>2.51</td>
<td>6.17</td>
<td>2.458</td>
<td>56</td>
</tr>
<tr>
<td>C₈K</td>
<td>Expt</td>
<td>455.9</td>
<td>4.960 (Ref. [61])</td>
<td>21.400 (Ref. [60])</td>
<td>4.315</td>
<td>47 (Ref. [62])</td>
</tr>
<tr>
<td></td>
<td>PBE</td>
<td>461.1</td>
<td>4.98</td>
<td>21.48</td>
<td>4.313</td>
<td>40</td>
</tr>
<tr>
<td></td>
<td>PBE+D2</td>
<td>452.6</td>
<td>4.97</td>
<td>21.12</td>
<td>4.249</td>
<td>64</td>
</tr>
</tbody>
</table>
TABLE VIII: Computed and experimental volume, lattice parameters, internal parameter z (see Fig. 5), bulk moduli, and cohesive energies for $\beta$-MoS$_2$ and NbSe$_2$ (space group $P6_3/mmc$).

<table>
<thead>
<tr>
<th>Compound</th>
<th>Method</th>
<th>$V$ (Å$^3$)</th>
<th>$a$ (Å)</th>
<th>$c$ (Å)</th>
<th>$c/a$</th>
<th>$z$</th>
<th>$B_0$ (GPa)</th>
<th>$\Delta E_{coh}$ (eV/atom)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\beta$-MoS$_2$</td>
<td>Expt (Ref. [65])</td>
<td>106.3</td>
<td>3.160</td>
<td>12.294</td>
<td>3.891</td>
<td>0.121</td>
<td>53.4 (Ref. [67])</td>
<td>$-5.18$ (Ref. [68])</td>
</tr>
<tr>
<td></td>
<td>PBE</td>
<td>128.8</td>
<td>3.18</td>
<td>14.68</td>
<td>4.616</td>
<td>0.143</td>
<td>2</td>
<td>$-5.12$</td>
</tr>
<tr>
<td></td>
<td>PBE+D2</td>
<td>109.4</td>
<td>3.19</td>
<td>12.42</td>
<td>3.893</td>
<td>0.125</td>
<td>39</td>
<td>$-5.37$</td>
</tr>
<tr>
<td>NbSe$_2$</td>
<td>Expt (Ref. [69])</td>
<td>127.9</td>
<td>3.440</td>
<td>12.482</td>
<td>3.628</td>
<td>0.116</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>PBE</td>
<td>145.0</td>
<td>3.49</td>
<td>13.78</td>
<td>3.948</td>
<td>0.128</td>
<td>6</td>
<td>$-4.95$</td>
</tr>
<tr>
<td></td>
<td>PBE+D2</td>
<td>132.6</td>
<td>3.46</td>
<td>12.76</td>
<td>3.688</td>
<td>0.118</td>
<td>42</td>
<td>$-5.27$</td>
</tr>
</tbody>
</table>

TABLE IX: Comparison of theoretical and experimental lattice parameters and bulk moduli for V$_2$O$_5$ (space group $Pmmm$).

<table>
<thead>
<tr>
<th>Method</th>
<th>$V$ (Å$^3$)</th>
<th>$a$ (Å)</th>
<th>$b$ (Å)</th>
<th>$b/a$</th>
<th>$c$ (Å)</th>
<th>$c/a$</th>
<th>$B_0$ (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>experiment (Ref. [70])</td>
<td>179.2</td>
<td>11.512</td>
<td>3.564</td>
<td>0.310</td>
<td>4.368</td>
<td>0.379</td>
<td>50 (Ref. [76])</td>
</tr>
<tr>
<td>PBE</td>
<td>199.0</td>
<td>11.54</td>
<td>3.57</td>
<td>0.310</td>
<td>4.83</td>
<td>0.419</td>
<td>10</td>
</tr>
<tr>
<td>PBE+D2</td>
<td>183.7</td>
<td>11.64</td>
<td>3.53</td>
<td>0.303</td>
<td>4.47</td>
<td>0.384</td>
<td>33</td>
</tr>
<tr>
<td>PW91 (Ref. [71])</td>
<td>195.1</td>
<td>11.65</td>
<td>3.57</td>
<td>0.306</td>
<td>4.69</td>
<td>0.403</td>
<td></td>
</tr>
<tr>
<td>PW91 (Ref. [72])</td>
<td>200.1</td>
<td>11.55</td>
<td>3.58</td>
<td>0.310</td>
<td>4.84</td>
<td>0.419</td>
<td></td>
</tr>
<tr>
<td>PW91 (Ref. [74])</td>
<td>193.8</td>
<td>11.65</td>
<td>3.57</td>
<td>0.306</td>
<td>4.66</td>
<td>0.400</td>
<td></td>
</tr>
<tr>
<td>PW91 (Ref. [73])</td>
<td>185.2</td>
<td>11.62</td>
<td>3.59</td>
<td>0.309</td>
<td>4.44</td>
<td>0.382</td>
<td></td>
</tr>
<tr>
<td>PW91 (Ref. [75])</td>
<td>182.6</td>
<td>11.53</td>
<td>3.60</td>
<td>0.312</td>
<td>4.40</td>
<td>0.382</td>
<td></td>
</tr>
</tbody>
</table>
TABLE X: Selected internal parameters for vanadium pentoxide. The labelling of oxygen atoms and the parameter \( d \) are shown in Fig. 6. The experimental values are from Ref. [70].

<table>
<thead>
<tr>
<th>Interatomic distance</th>
<th>Expt</th>
<th>PBE</th>
<th>PBE+D2</th>
</tr>
</thead>
<tbody>
<tr>
<td>V-O(1)</td>
<td>1.58</td>
<td>1.61</td>
<td>1.61</td>
</tr>
<tr>
<td>V-O(2)</td>
<td>1.78</td>
<td>1.79</td>
<td>1.78</td>
</tr>
<tr>
<td>V-O(3)</td>
<td>1.88, 2.02</td>
<td>1.89, 2.04</td>
<td>1.88, 2.06</td>
</tr>
<tr>
<td>( d )</td>
<td>2.79</td>
<td>2.86</td>
<td>3.23</td>
</tr>
</tbody>
</table>

TABLE XI: Computed and experimental [77] equilibrium volume, lattice constants, parameter \( u \) specifying the basis within the elementary cell, and bulk modulus for selenium and tellurium (space group \( hP3 \)).

<table>
<thead>
<tr>
<th>Compound</th>
<th>Method</th>
<th>V (( \text{Å}^3 ))</th>
<th>a (( \text{Å} ))</th>
<th>c (( \text{Å} ))</th>
<th>c/a</th>
<th>u (GPa)</th>
<th>( B_0 ) (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Se</td>
<td>Expt</td>
<td>81.9</td>
<td>4.368</td>
<td>4.958</td>
<td>1.135</td>
<td>0.225</td>
<td>14.9</td>
</tr>
<tr>
<td></td>
<td>PBE</td>
<td>89.3</td>
<td>4.52</td>
<td>5.04</td>
<td>1.115</td>
<td>0.219</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td>PBE+D2</td>
<td>80.5</td>
<td>4.27</td>
<td>5.10</td>
<td>1.194</td>
<td>0.232</td>
<td>8</td>
</tr>
<tr>
<td></td>
<td>PB-US (Ref. [78])</td>
<td>87.3</td>
<td>4.46</td>
<td>5.08</td>
<td>1.140</td>
<td>0.224</td>
<td>7</td>
</tr>
<tr>
<td>Te</td>
<td>Expt</td>
<td>101.7</td>
<td>4.451</td>
<td>5.926</td>
<td>1.331</td>
<td>0.263</td>
<td>19.4</td>
</tr>
<tr>
<td></td>
<td>PBE</td>
<td>104.8</td>
<td>4.50</td>
<td>5.96</td>
<td>1.324</td>
<td>0.270</td>
<td>18</td>
</tr>
<tr>
<td></td>
<td>PBE+D2</td>
<td>98.1</td>
<td>4.33</td>
<td>6.04</td>
<td>1.395</td>
<td>0.277</td>
<td>23</td>
</tr>
<tr>
<td></td>
<td>PB-US (Ref. [78])</td>
<td>108.3</td>
<td>4.57</td>
<td>5.99</td>
<td>1.310</td>
<td>0.269</td>
<td>18</td>
</tr>
</tbody>
</table>
TABLE XII: Selected internal coordinates for selenium and tellurium structures: intra-chain distance ($d_1$), bonding angle ($\theta$), and inter-chain distance ($d_2$). The experimental data are from Ref. [77].

<table>
<thead>
<tr>
<th>Compound</th>
<th>Method</th>
<th>$d_1$ (Å)</th>
<th>$\theta$ (°)</th>
<th>$d_2$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Se</td>
<td>Expt</td>
<td>2.37</td>
<td>103.2</td>
<td>3.44</td>
</tr>
<tr>
<td></td>
<td>PBE</td>
<td>2.40</td>
<td>103.5</td>
<td>3.57</td>
</tr>
<tr>
<td></td>
<td>PBE+D2</td>
<td>2.42</td>
<td>104.0</td>
<td>3.37</td>
</tr>
<tr>
<td>Te</td>
<td>Expt</td>
<td>2.83</td>
<td>103.3</td>
<td>3.49</td>
</tr>
<tr>
<td></td>
<td>PBE</td>
<td>2.89</td>
<td>101.9</td>
<td>3.50</td>
</tr>
<tr>
<td></td>
<td>PBE+D2</td>
<td>2.89</td>
<td>103.2</td>
<td>3.40</td>
</tr>
</tbody>
</table>

TABLE XIII: Comparison of theoretical and experimental lattice parameters and bulk moduli for cellulose I$\beta$ (monoclinic lattice, space group $P2_1$). Structural experimental data are from Ref. [79].

<table>
<thead>
<tr>
<th>Method</th>
<th>$V$ ($\text{Å}^3$)</th>
<th>$a$ (Å)</th>
<th>$b$ (Å)</th>
<th>$c$ (Å)</th>
<th>$b/a$</th>
<th>$c/a$</th>
<th>$\gamma$ (°)</th>
<th>$B_0$ (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>experiment</td>
<td>658.3</td>
<td>7.784</td>
<td>8.201</td>
<td>10.380</td>
<td>1.054</td>
<td>1.333</td>
<td>96.6</td>
<td></td>
</tr>
<tr>
<td>PBE</td>
<td>744.9</td>
<td>8.70</td>
<td>8.23</td>
<td>10.46</td>
<td>0.946</td>
<td>1.202</td>
<td>95.5</td>
<td>6</td>
</tr>
<tr>
<td>PBE+D2</td>
<td>642.5</td>
<td>7.65</td>
<td>8.14</td>
<td>10.39</td>
<td>1.064</td>
<td>1.358</td>
<td>96.8</td>
<td>16</td>
</tr>
</tbody>
</table>
TABLE XIV: Equilibrium lattice constants and bulk moduli for silicon, diamond, and NaCl crystals, compared with experimental data as presented in Ref. [86].

<table>
<thead>
<tr>
<th>Compound</th>
<th>Method</th>
<th>a (Å)</th>
<th>$B_0$ (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>Expt</td>
<td>5.416</td>
<td>99.2</td>
</tr>
<tr>
<td></td>
<td>PBE</td>
<td>5.47</td>
<td>89</td>
</tr>
<tr>
<td></td>
<td>PBE+D2</td>
<td>5.41</td>
<td>98</td>
</tr>
<tr>
<td>diamond</td>
<td>Expt</td>
<td>3.543</td>
<td>443</td>
</tr>
<tr>
<td></td>
<td>PBE</td>
<td>3.57</td>
<td>434</td>
</tr>
<tr>
<td></td>
<td>PBE+D2</td>
<td>3.56</td>
<td>441</td>
</tr>
<tr>
<td>NaCl</td>
<td>Expt</td>
<td>5.565</td>
<td>26.6</td>
</tr>
<tr>
<td></td>
<td>PBE</td>
<td>5.70</td>
<td>24</td>
</tr>
<tr>
<td></td>
<td>PBE+D2</td>
<td>5.66</td>
<td>32</td>
</tr>
</tbody>
</table>

TABLE XV: Lattice parameters and bulk modulus for siliceous chabazite (trigonal lattice, $R\bar{3}m$), comparison of experiment and DFT calculations. Experimental structural data are from Ref. [81], bulk modulus from Ref. [82].

<table>
<thead>
<tr>
<th>Method</th>
<th>V (Å³)</th>
<th>a (Å)</th>
<th>α (°)</th>
<th>$B_0$ (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>experiment</td>
<td>796.1</td>
<td>9.291</td>
<td>93.9</td>
<td>62</td>
</tr>
<tr>
<td>PBE</td>
<td>812.0</td>
<td>9.35</td>
<td>94.1</td>
<td>68</td>
</tr>
<tr>
<td>PBE+D2</td>
<td>809.1</td>
<td>9.34</td>
<td>94.1</td>
<td>72</td>
</tr>
</tbody>
</table>
FIG. 1: Energy versus volume curves for graphite computed with PBE and PBE+D2 approach. The PBE curve has been shifted along the E axis in order to facilitate the comparison. The arrows indicate the volumes of structures relaxed using the full lattice optimization: 43.2 Å$^3$ (PBE) and 34.2 Å$^3$ (PBE+D2).

FIG. 2: Structure of cytosine, projections into $ab$ and $ac$ planes.
FIG. 3: Molecule of cytosine.

FIG. 4: Top and side views of potassium graphite structure.

FIG. 5: Side view of the crystalline structure of molybdenum disulfide. The parameter $z$ is displacement of sulfur with respect to molybdenum atoms along the lattice vector $c$. 
FIG. 6: Side and top views of the crystalline structure of vanadium pentoxide $V_2O_5$. Position of three symmetry inequivalent oxygen atoms and the nearest interlayer vanadium - oxygen distance ($d$) are shown.

FIG. 7: Side view of the crystalline selenium, the interatomic distances $d_1$, and $d_2$, and bonding angle $\theta$ are shown.

FIG. 8: Structure of cellulose I$\beta$, projections into $ab$ and $bc$ planes.