B3LYP augmented with an empirical dispersion term (B3LYP-D*) as applied to molecular crystals

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The B3LYP method augmented with a damped empirical dispersion term ($-f(R)C_6/R^6$) is shown to yield structures and cohesive energies, for a representative set of molecular crystals, in excellent agreement with experimental data. Vibrational lattice modes of crystalline urea are also reported to be very close to experiment. The role of the damping function in scaling the dispersion contribution has been analyzed as well as the relevance of the BSSE in the prediction of structure and cohesive energy.

Introduction

Ab initio modelling of molecular crystals is of interest for crystal structure prediction, relative stability of different polymorphs, crystal growth and supramolecular chemistry with relevant applications in many fields as crystal engineering and pharmaceutical industry. The critical issue in molecular crystals simulation is the proper description of noncovalent interactions between molecules (i.e. hydrogen bonding, dispersive interactions, dipolar effects, and so forth) that dictate the crystalline structure and the thermodynamic properties controlling phase transitions. In this respect, density functional theory (DFT) methods have been widely used in the ab initio modelling of molecular crystals but it has been shown that they often fail to adequately describe dispersive interactions. To overcome this problem, different strategies have been proposed to improve current DFT methods: (i) fully ab-initio approaches (i.e. non-empirical), (ii) the reparameterization of existing functionals and (iii) the inclusion of empirical terms. Recently, this latter approach has been the subject of a renewed interest and several attempts have been reported to use pair-wise attraction terms of the form $-f(R)C_n/R^n$ (n=6,7,8,…) for both molecular complexes[1-12] and extended systems[13-18]. The proposed corrections differ in the form of the damping function $f(R)$ and the atom-atom dispersion coefficients C_n.

In this work, we focus on the empirical $-f(R)C_6/R^6$ correction to DFT methods recently proposed by Grimme[3, 4] for molecular systems. Grimme defined a general set of parameters and used an optimized scaling factor to adjust the dispersion correction for each DFT method. The model has been demonstrated to be successful in dealing with small molecular adducts, π-stacking, and large complexes (e.g. DNA base pairs) of interest for biological systems[5-7, 12]. The present aim is to use the Grimme empirical model in combination with the B3LYP[19-21] hybrid method (hereafter referred as B3LYP-D) and assess the trasferability of such a model to the case of molecular crystals. Hybrid functionals and in particular the B3LYP methods, have been demonstrated to give accurate results for energetics, structure and vibrational properties of molecules[22] and solids[23]. They give better results than LDA and GGA functionals and are still slightly superior than recently proposed mGGA functionals. Although, recently, some of us have shown that B3LYP fails to give the correct structure of crystalline urea with large deviations from experiment (up to 5%) for the lattice parameters because of the missing contribution of dispersive forces[24].

The Grimme empirical model has been implemented in the CRYSTAL code, a periodic ab initio program based on an atom-centered (Gaussian) basis set. In this respect, our approach is similar to that recently adopted by Feng and Li[16] where they used the B3LYP functional combined with a different empirical dispersion correction to predict the cohesive energy of organic molecular crystals. Here, at difference with ref. 16, we also assess the B3LYP-D model chemistry in predicting the fully relaxed crystalline structure and the vibrational frequencies at the Γ point.

Results are first reported for the cohesive energy of a set of 14 molecular crystals ranging from hydrogen bonded to dispersion bonded crystals (i.e. NH_3, acetylene, CO_2, urea, urotropine, propane, benzene, naphthalene, formamide, formic acid, 1,4-dichloro-benzene, 1,4-dicyano-benzene, succinic anhydride and boric acid). Among them, six molecular crystals have then been fully optimised. Finally, for crystalline urea, the vibrational lattice modes at the Γ point are also reported. A systematic comparison with available experimental results is carried out to assess the accuracy of the computed results. Since Gaussian-type basis sets were used in the present work, particular attention has been paid to the basis set dependence and the role of the basis set superposition error (BSSE).

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† Electronic Supplementary Information (ESI) available: Full set of computed cohesive energies and references to experimental data (Table S1). Details of the adopted strategy to rescale the atomic van der Waals radii of the modified Grimme model: B3LYP-D* (Table S2 and Figure S1). See http://dx.doi.org/10.1039/b715018k/

Computational details

All B3LYP-D calculations have been carried out by using a development version of the periodic ab-initio code CRYSTAL06[25]. According to ref. [3, 4], an atom-atom additive damped empirical potential of the form $-f(R)C_6/R^6$ were used to include long-range dispersion contributions to the computed ab initio DFT total energy and gradients at the B3LYP[19-21] level of theory:

$$E_{B3LYP\text{-}D}=E_{B3LYP}+E_{Disp}$$

where E_{Disp} is the empirical term

$$E_{Disp}=-s_6\sum_{\mathbf{g}}\sum_{ij}{}' f_{dmp}(R_{ij,\mathbf{g}})\frac{C_6^{ij}}{R_{ij,\mathbf{g}}^6}$$

Here, the summation is over all atom pairs and $\boldsymbol{g}$ lattice vectors with the exclusion of the $i=j$ contribution (i.e. self interaction) for $\boldsymbol{g}=0$, C_6^{ij} is the dispersion coefficient for the pair of atoms i and j, s_6 is a scaling factor that depends on the adopted DFT method (s_6=1.05 for B3LYP[4]) and $R_{ij,\boldsymbol{g}}$ is the interatomic distance between atoms i in the reference cell and j in the neighbouring cells at distance $|\boldsymbol{g}|$. A cutoff distance of 25.0 Å was used to truncate the summation over lattice vectors which corresponds to an estimated error of less than 0.02 kJ/mol on computed cohesive energies with respect to larger cutoffs. A damping function was used to avoid near-singularities for small interatomic distances:

$$f_{dmp}\left(R_{ij,\mathbf{g}}\right)=\frac{1}{1+e^{-d\left(R_{ij,\mathbf{g}}/R_{vwd}-1\right)}}$$

where R_{vdw} is the sum of atomic van der Waals radii and d determines the steepness of the damping function (d=20)[4]. The role of the damping functions is crucial and will be further discussed below. Van der Waals radii and atomic C_6 coefficients were taken from Table 1 of ref. 4. From the latter, the C_6^{ij} dispersion coefficients were computed by using a geometric mean.

B3LYP calculations were carried out by using two different molecular all-electron basis sets, namely: the standard 6-31G(d,p)[26] and a TZP basis set devised by Ahlrichs and co-workers[27] with the latter being quite effective to reduce BSSE in calculations on molecular crystals[28]. The level of accuracy in evaluating the Coulomb and exchange series is controlled by five thresholds[25], for which values of 10^{-7}, 10^{-7}, 10^{-7}, 10^{-7}, 10^{-16} were used for the Coulomb and the exchange series. The DFT exchange-correlation contribution is evaluated by numerical integration over the cell volume[29]. Radial and angular points of the atomic grid are generated through Gauss-Legendre and Lebedev quadrature schemes. A grid pruning was adopted, as discussed in ref [29]. In the present study a (75,974)p grid has been used that contains 75 radial points and a variable number of angular points, with a maximum of 974 on the Lebedev surface in the most accurate integration region. The condition for the SCF convergence was set to 10^{-7} on the energy difference between two subsequent cycles. The shrinking factor of the reciprocal space net for each system was set to define a mesh of points in the irreducible Brillouin zone for which the total energies are fully converged.

Starting from the experimental crystal structures and fixing the symmetry, a full relaxation of both lattice parameters and atomic coordinates by means of analytical energy gradients[30-32] was carried out. The geometry optimisation is performed by means of a quasi-Newton algorithm in which the quadratic step (BFGS Hessian updating scheme) is combined with a linear one (parabolic fit) as proposed by Schlegel. Convergence is tested on the RMS and the absolute value of the largest component of the gradients and the estimated displacements. The threshold for the maximum force, the RMS force, the maximum atomic displacement, and the RMS atomic displacement on all atoms have been set to 0.00045, 0.00030, 0.00180 and 0.00120 a.u., respectively. The optimisation is considered complete when the four conditions are simultaneously satisfied. The crystal symmetry was maintained during the whole optimisation process.

The cohesive energy was computed as :

$$\Delta E=E(bulk)/Z-E(mol)$$

where E(bulk) is the total energy of the unit cell and must be referred to the number, Z, of molecules in the unit cell, and E(mol) is the total energy of the isolated molecule in the gas phase. Computed data were corrected for the BSSE through the counterpoise method[33]. Computed cohesive energies were compared with lattice energies estimated from experimental sublimation energies[34] by adding a constant contribution of 2RT[35] (i.e. $-\Delta E=\Delta H^0_{sub}(T)+2RT$) to approximate the zero-point energy and thermal corrections to 298 K.

For crystalline urea, vibrational frequencies at the Γ point[29] were computed, within the harmonic approximation, by diagonalizing the mass-weighted Hessian matrix. Second derivatives are calculated numerically by using analitycal first derivatives and finite displacements of the atomic positions. A three-point formula was used with a step amplitude equal to 0.001 Å.

Results and Discussions

Cohesive energies

The cohesive energy of a set of molecular crystals ranging from dispersion bonded to hydrogen bonded crystals (i.e. NH_3, acetylene, CO_2, urea, urotropine, propane, benzene, naphthalene, formamide, formic acid, 1,4-dichloro-benzene, 1,4-dicyano-benzene, succinic anhydride and boric acid) have been computed at the B3LYP/6-31G(d,p) level of theory without and with the Grimme empirical dispersion correction (i.e. B3LYP-D Grimme). Atomic positions of the crystalline structures were fully relaxed at the B3LYP/6-31G(d,p) level by fixing the cell parameters at their experimental values. Results are shown in Figure 1 where BSSE corrected cohesive energies are compared to the experimental lattice energies while Table 1 reports a statistical analysis on the computed data. The full set of results along with references to the crystallographic data of the studied systems, is reported as electronic supplementary information.

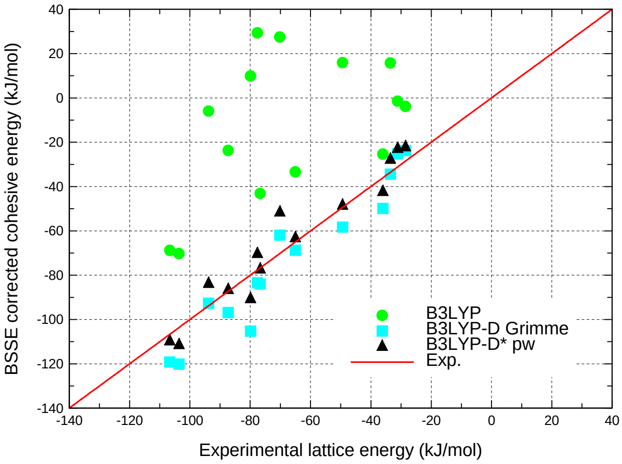

Fig. 1 Comparison between BSSE corrected cohesive energies and experimental lattice energies for the studied systems. Reported results are obtained at the B3LYP/6-31G(d,p) level and augmented with the original Grimme empirical dispersion correction (B3LYP-D Grimme) and with the modified version proposed in the present work (B3LYP-D* pw).

As can be seen from Figure 1, the dispersion correction is crucial to arrive at a reasonable agreement with experiment. In fact, the pure B3LYP method gives results that are rather poor. The cohesive energies are generally underestimated and in many cases, mainly for dispersion bonded molecular crystals (e.g. propane, C_6H_6, naphthalene, ...) they becomes repulsive. Large positive deviations from experiment are observed for all systems, with a mean absolute deviation (MAD) of 54.4 kJ/mol and a maximum error of 107.0 kJ/mol for naphthalene. The inclusion of the dispersion term in the original parameterization proposed by Grimme leads to a dramatic improvement and a good agreement with experimental data. Computed results are now less spread and the MAD decreases to 8.9 kJ/mol. However, a clear tendency to overestimate the cohesive energy (MD=-6.0 kJ/mol) is observed, especially for hydrogen bonded molecular crystals. This aspect cannot be undervalued because it could affect the geometry optimization of the crystalline structure leading to underestimated lattice parameters, as it will be discussed later on. The overestimation can be explained by considering two aspects. On one hand, at variance with molecular complexes, for which the empirical term was calibrated, in molecular crystals the intermolecular contacts are shorter and the overlap between charge density distributions is larger. This feature is controlled by the damping function that probably is too short-range for crystalline systems. On the other hand, the original parametrization by Grimme contains the s_6 scaling factor that rescales the whole contribution that, for B3LYP, it is increased by a factor 1.05[4]. The results shown in Figure 1 then indicate that the overall effect is an unbalanced estimation of the dispersion contribution. To overcome this problem, we followed the strategy suggested by Jurecka *et al.*[7] Instead of rescaling the whole $-f(R)C_6/R^6$ empirical correction, we rescaled the adopted atomic van der Waals radii that enter in the form of the damping function to make it active in a more long-range region, thus decreasing the dispersion contribution. This procedure is also physically sound because it includes the dispersion contribution only in the regions where the B3LYP method does not contribute to the intermolecular interactions. Another crucial aspect is the van der Waals radius of hydrogen. Its value is more delicate because it determines the penetration of the damping function in balancing the dispersion contribution for hydrogen bonded and dispersion bonded molecular crystals and it was subject to a larger rescaling than the other atomic species. Therefore, we propose to modify the original Grimme model setting the s_6 scaling factor to 1.00 and applying a scaling factors of 1.05 and 1.30 to the atomic van der Waals radii of heavy atoms and hydrogen of Table 1 in ref. 4, respectively. Proposed scaling factors were determined from a manual procedure by progressively increasing the atomic van der Waals radii and trying to find the best agreement between computed and experimental data. For sake of conciseness, details on the calibration strategy are reported as electronic supplementary information. Results for the present correction (i.e. hereafter referred as B3LYP-D*) applied to the studied molecular crystals are also reported in Figure 1 and analyzed in Table 1. The adopted rescaling procedure leads to an enhanced agreement with respect to experimental data (MAD=6.3 kJ/mol) and to a better balance in the performance of the B3LYP-D* model chemistry between hydrogen bonded and dispersion-bonded molecular crystals (MD=2.2 kJ/mol). It is worthy to note that, for some of the systems studied in the present work, B3LYP-D* results agree with those recently reported by Feng and Li[16], even if they used a different form of the damping function and calculations were carried out with a 6-21G(d,p) basis set.

Table 1 Statistical analysis on the computed cohesive energies (in kJ/mol) for the studied molecular crystals at the B3LYP/6-31G(d,p) level of theory and combined with the original Grimme empirical dispersion correction (B3LYP-D Grimme) and the present modified version (B3LYP-D* pw) with respect to experimental data.

	B3LYP	B3LYP-D (Grimme)	B3LYP-D* (pw)
MD[b]	54.4	-6.0	2.2
MAD[c]	54.4	8.9	6.3
Min[d]	10.6	-25.4	-10.8
Max[e]	107.0	8.3	18.6

[a] The full set of data is reported in Table S1†. [b] Mean deviation. [c] Mean absolute deviation. [d] Minimum deviation. [e] Maximum deviation

Structural results

We expect our modification of the Grimme model based on energetics to be reasonable. However, the comparison of the computed cohesive energy with experiment can be questionable in two respects: (i) the accuracy of the reference calorimetric data that can have error bars larger than ±4.0 kJ/mol and (ii) the adopted approximation to derive the lattice energy by adding a constant contribution (i.e. 2RT) to take ZPE and thermal corrections into account. We then extended the assessment not only to energetics but also to structural information. In fact, accurate low temperature crystallographic data are available for comparison. Among studied molecular crystals, six systems were selected to be fully optimized. Optimized lattice parameters and

Table 2 Computed lattice parameters (in Å), unit cell volume (in Å^3) and cohesive energies (in kJ/mol) of the studied molecular crystals at the B3LYP level of theory and B3LYP augmented with the original (B3LYP-D) and modified (B3LYP-D*) Grimme empirical dispersion correction as compared to experimental data.

		B3LYP		B3LYP-D (Grimme)		B3LYP-D* (pw)		Exp.[c]
		6-31G(d,p)	TZP	6-31G(d,p)	TZP	6-31G(d,p)	TZP	
NH_3	a	5.200 (3.0)[a]	5.256 (4.1)	4.754 (-5.8)	4.844 (-4.0)	4.924 (-2.5)	4.987 (-1.2)	5.048
	V	140.6 (9.3)	145.2 (12.9)	107.4 (-16.5)	113.7 (-11.6)	119.4 (-7.2)	124.0 (-3.6)	128.6
	ΔE	-27.1 [15.9][b]	-23.8 [4.7]	-47.2 [20.6]	-45.8 [6.0]	-41.5 [18.1]	-38.9 [5.5]	-36.0
C_2H_2 cubic	a	6.156 (1.0)	6.634 (8.7)	5.643 (-7.5)	5.766 (-5.4)	5.825 (-4.5)	5.970 (-2.0)	6.094
	V	233.2 (3.1)	292.0 (29.0)	179.7 (-20.9)	191.7 (-15.3)	197.7 (-13.0)	212.7 (-6.0)	226.3
	ΔE	-4.4 [11.6]	-4.4 [0.9]	-25.1 [16.1]	-23.5 [1.1]	-22.0 [14.3]	-20.3 [1.0]	-28.5
CO_2	a	5.708 (1.5)	5.894 (4.8)	5.427 (-3.5)	5.481 (-2.6)	5.496 (-2.3)	5.566 (-1.0)	5.624
	V	186.0 (4.5)	204.7 (15.1)	159.8 (-10.2)	164.6 (-7.4)	166.0 (-6.7)	172.4 (-3.1)	177.9
	ΔE	-3.8 [13.6]	-6.2 [2.3]	-23.6 [17.9]	-28.3 [3.0]	-22.2 [17.0]	-25.4 [2.9]	-31.1
Urotropine	a	7.327 (5.8)	7.453 (7.6)			6.861(-1.0)	6.879 (-0.7)	6.927
	V	393.4 (18.3)	414.0 (24.5)			323.0 (-2.8)	325.5 (-2.1)	332.4
	ΔE	-15.3 [21.8]	-13.5 [4.3]			-91.5 [34.5]	-94.1 [7.0]	-79.9
Urea	a	5.675 (2.0)	5.841 (5.0)			5.460 (-1.9)	5.541 (-0.4)	5.565
	c	4.682 (0.0)	4.710 (0.5)			4.647 (-0.8)	4.672 (-0.2)	4.684
	V	150.8 (3.9)	160.7 (10.7)			138.6 (-4.5)	143.5 (-1.1)	145.1
	ΔE	-66.1 [32.8]	-67.9 [6.8]			-103.1 [37.2]	-104.9 [8.1]	-103.6
C_6H_6	a	8.592 (16.7)	n/a			7.340 (-0.3)	7.368 (0.1)	7.360
	b	8.674 (-7.5)	n/a			9.189 (-2.0)	9.359 (-0.3)	9.375
	c	8.588 (28.1)	n/a			6.589 (-1.7)	6.686 (-0.4)	6.703
	V	640.0 (38.4)	n/a			444.4 (-3.9)	461.0 (-0.3)	462.5
	ΔE	-5.8 [8.9]	n/a			-47.9 [20.1]	-46.3 [1.9]	-49.8

[a] Percentage deviation from experimental data in parentheses. [b] BSSE correction (in kJ/mol) is reported in square brackets. [c] Details and references to experimental data are reported in Table S1†.

corresponding cohesive energies are gathered in Table 2. As already pointed out by Jurecka *et al.*[7] for molecular complexes, the BSSE is very important. When using small basis sets, as the 6-31G(d,p), it artificially gives binding energy where there is none and it may partly compensate the missing dispersion attractive interaction thus yielding structures in fortuitous agreement with experiment[28]. This implies that the inclusion of the empirical dispersion correction has to be carefully checked to avoid an underestimation of the lattice constants. Therefore, to reduce the BSSE, a TZP basis set[27] was used. For the simplest studied molecular crystals (i.e. NH_3, C_2H_2, CO_2) calculations were performed with both the original Grimme model and its modified version proposed in the present work.

From results reported of Table 2, it can be seen that at the B3LYP level of theory: (i) lattice parameters are largely overestimated with a maximum deviation of 30% for crystalline benzene, while the cohesive energies are definitely underestimated; (ii) the use of the TZP basis set dramatically reduces the BSSE with respect to 6-31G(d,p). As a consequence, computed lattice constants are even more overestimated and for benzene geometry optimization did not find any minimum; (iii) the comparison between the two adopted basis sets confirms that the BSSE corrected cohesive energies show a small basis set dependence.

As expected from previous discussion, the inclusion of the empirical dispersion correction in the original proposal by Grimme causes a marked underestimation of the lattice parameters, up to -7.5% with the 6-31G(d,p) basis set, while a significant improvement is obtained for the cohesive energy although not properly balanced. In fact, for NH_3 which is dominated by hydrogen bonding, the cohesive energy is overestimated by ~10 kJ/mol. This confirms that the sum of BSSE and dispersion correction adds too much attraction between the molecule so that it is very delicate when a small basis set is adopted. The TZP basis set reduces the BSSE to less than 10% of the cohesive energy although it demonstrates that the original Grimme model still tends to overestimate the dispersion contribution, as shown before.

Instead, the use of the modified B3LYP-D* model chemistry leads to better balanced results for both lattice constants and cohesive energies as well as for hydrogen bonded and dispersion bonded molecular crystals. B3LYP-D*/TZP data nicely agree with experiment with remarkably small deviations (~1%) on the lattice parameters for two quite different molecular crystals as urea and benzene. For cubic acetylene, the deviation is slightly larger but it decreases to -0.5% when the extrapolated value of the lattice constant at 0 K (i.e. 5.998 Å) is used. Computed unit cell volumes favourably compare with those obtained by Neumann and Perrin[14] for a larger set of molecular crystals by using a similar dispersion correction term at the PW91 level of theory within a planewave/pseudopotential theoretical frame. Reported percentage deviations[14] with respect to experiment for cubic acetylene (extrapolated at 0 K), urotropine, urea and benzene are: -0.4, -1.3, -3.1 and 0.7, respectively, very close to the corresponding B3LYP-D*/TZP values of Table 2, i.e. -1.4, -2.1, -1.1 and -0.3.

Table 3 Harmonic vibrational lattice modes (in cm^{-1}) of crystalline urea computed at the B3LYP/TZP level of theory for both fully relaxed and at fixed experimental cell parameters and B3LYP/TZP combined with the modified Grimme empirical dispersion correction (B3LYP-D*) of the present work compared with experimental data[36].

Mode	Type^{a,b}	B3LYP	B3LYP (exp.)	B3LYP-D* (pw)	Exp.^{c}
ν_1	B_1 (R$_z$)	61	63	72	63
ν_2	A_2 (R$_z$)	50	79	95	-
ν_3	E (T$_{x,y}$)	93	110	121	108
ν_4	A_1 (T$_z$)	103	132	135	119
ν_5	E (R$_y$)	130	169	174	156
ν_6	E (R$_x$)	177	214	222	204

[a] Symmetry: E modes are infrared and Raman active, A_1 and B_1 modes are Raman active and A_2 modes are inactive. [b] Libration mode type: R=rotational and T=translational; The z axis is parallel to the c-axis, and the x and y axes are inclined at 45° with respect to the a and b crystallographic axes. [c] Values extrapolated at 0 K from Raman data at 298 K and 100 K.

Overall results show that the modified Grimme model when used in combination with a triple-zeta basis set is sound and reliable.

Vibrational lattice modes of crystalline urea

As a further test for the validation of the empirical dispersion correction, we considered the prediction of vibrational lattice modes in molecular crystals that can be significantly affected by the proper description of the intermolecular interactions. Table 3 reports the comparison between computed harmonic lattice modes of crystalline urea and the experimental data at 0 K derived through a linear extrapolation of Raman data obtained at 100 K and 298 K[36]. Since there are two molecules in the unit cell, the number of vibrational lattice modes (external modes) is 12, corresponding to six translational (T, three of them are zero at the Γ point) and six rotational (R, librations) degrees of freedom. From Table 3, it can be seen an overall agreement between computed and experimental data. At the B3LYP level, all frequencies are lower than experimental ones because of the overestimation of the cell parameters. The missing attractive dispersive forces lead to softer vibrational lattice modes. For comparison, we also reported data for the calculation at fixed experimental cell. All values increase because of the constraint on the cell that keeps the molecules closer to each other. When the empirical dispersion correction is added the computed frequencies slightly increase because the dispersion forces make the intermolecular interactions stronger. This is more evident for the E lattice modes that involve vibrations along the a and b lattice parameters where the dispersion forces play a more relevant role for the correct description of the crystalline structure[28]. We consider the computed data in fairly good agreement with experiment with the small overestimation being likely due to anharmonicity.

Conclusions

In this brief account, we reported on the implementation and validation of the Grimme empirical dispersion correction[4] as combined to the B3LYP method for periodic systems. A modification of the original parameterisation has been proposed that allows to obtain an excellent agreement for cohesive energies and structures of a representative set of molecular crystals and a better balance between hydrogen bonded and dispersion bonded molecular crystals. Vibrational lattice modes of crystalline urea have also been nicely reproduced.

The basis set dependence of the computed data have been explored to investigate the role of the BSSE. It is shown that BSSE deteriorates the results when small basis sets are adopted. Therefore, larger basis sets as the Ahlrichs TZP one must be adopted, although they can be more computationally demanding. The cost of the calculation might be reduced by combining the empirical correction with a pure GGA functional like the B97-D originally proposed by Grimme[4]. Work is under way to implement it in the CRYSTAL06 code.

Overall results are then very promising and the application of this empirical dispersion term deserves to be further investigated.

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