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L. Maschio, D. Usvyat, B. Civalleri

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Ab initio study of van der Waals and hydrogen-bonded molecular crystals with a periodic local-MP2 method.

Lorenzo Maschio* Denis Usvyat † Bartolomeo Civalleri‡

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Abstract

We have studied ab-initio the cohesive energy of a set of five molecular crystals with CRYSCOR, a new program implementing a periodic local second-order Møller-Plesset perturbation theory (LMP2) method. The set of studied crystals includes hydrogen-bonded (Ice XI, NH₃, Formic acid) and van der Waals (CO₂, C₂H₂) crystals. Polarization-augmented triple-zeta quality basis set has been used throughout. The method allows us to obtain cohesive energies in a good agreement with the experimental values. Results are also compared to those obtained with a recently proposed B3LYP augmented with an empirical dispersion term (D*) specifically tuned for bulk molecular crystals, and with those obtained through a Spin Component Scaling of the LMP2 results. We finally analyze the correlation contribution to the cohesive energy by separating the intramolecular and intermolecular contribution, according to the distance between correlated electrons, allowing for an interesting insight on the role of weak interactions in the studied systems. In this respect, crystalline Formic acid is analyzed in more detail. The

*Dipartimento di Chimica IFM, and Centre of Excellence NIS (Nanostructured Interfaces and Surfaces), Università di Torino, via Giuria 5, I-10125 Torino (Italy) E-mail: lorenzo.maschio@unito.it

†Institute for Physical and Theoretical Chemistry, Universität Regensburg, Universitätsstrasse 31, D-93040 Regensburg (Germany)

‡Dipartimento di Chimica IFM, and Centre of Excellence NIS (Nanostructured Interfaces and Surfaces), Università di Torino, via Giuria 5, I-10125 Torino (Italy)

investigation of the long range contribution to the cohesive energy also allows us to draw a correspondence between the ab-initio LMP2 and empirical approaches used to describe dispersion interactions.

1 Introduction

Molecular crystals certainly represent a tough challenge for the standard tools of modern solid state quantum chemistry. The main difficulties in trying to obtain a correct description of weakly-bound systems are due to the essential role that dispersive forces play, when covalent and ionic binding is absent, since the long-range forces cannot be correctly described neither by standard Density Functional Theory (DFT) nor Hartree-Fock (HF) approaches. The possibility of ab-initio quantum chemical modeling of such systems is of key importance for an accurate theoretical estimation of the cohesive energies, equilibrium geometries, *etc.*, as well as prediction of relative stabilities of different phases.

The technological interest of molecular crystals covers a wide range of areas, from engineering to pharmaceutical chemistry to astrochemistry¹ and is generally beyond this discussion. On the other hand, a fundamental understanding of their peculiar physical and chemical properties is of not less scientific interest. Great efforts in the scientific community to tackle this problem are witnessed by the increasing number of works on this topic in recent literature. Different approaches have been proposed:

- (i) The reparametrization and recalibration of existing DFT functionals;² this also includes range-separated hybrids that combine the best features of DFT and HF,^{3,4} and inclusion of non local functionals for van der Waals interactions.⁵
- (ii) The introduction of an empirical correction to take into account dispersive forces. A proposal by Grimme⁶ to augment DFT methods with an empirical $-C_6/R^6$ term, has been recently adapted by one of us for the description of molecular crystals.⁷
- (iii) The use of fully ab initio correlation approaches, adapted for periodic crystals,

but based on finite models.⁸⁻¹⁴ These methods, mostly based on Stoll's incremental scheme^{15,16} or on similar ideas,¹⁷ are generally quite powerful, but often not easily transferable from one system to another.

- (iv) Fully periodic ab initio correlation methods, using plane wave¹⁸ or Gaussian-type basis.^{19,20}

This paper mainly deals with the items (ii) and (iv), with particular focus on the last one.

We have used a pre-release version of the new CRYSCOR09 program,²⁰⁻²⁴ developed by some of us and collaborators, to study of a set of different molecular crystals. The program presently implements a periodic variant of the second-order Møller-Plesset perturbation theory (MP2), that is the first step in the hierarchy of wavefunction-based post-Hartree-Fock methods, and is based on the "local" approach first proposed by Pulay²⁵ and further developed by Werner, Schütz and others.²⁶ This approach, which exploits the locality of the correlation effects, has led to linear scaling of the computational cost with the size of the system.

CRYSCOR employs the periodic Hartree-Fock solution in the basis of Gaussian-type orbitals (GTO) provided by the CRYSTAL code.²⁷ The possibility to express this solution via symmetry adapted Wannier functions,^{28,29} provides a suitable starting point for the local correlation treatment. It also employs an approximate integral evaluation techniques, like density fitting (DF),³⁰ which makes correlation calculations feasible for systems presently up to 50 atoms in the unit cell and relatively large basis sets.^{24,31,32} CRYSCOR is capable to handle almost all systems that can be studied with CRYSTAL, including periodicity in 3D, 2D, 1D and 0D. The LMP2 code is though limited to the study of closed-shell nonconducting crystals, due to the need of a localization step, and the limitations of the MP2 perturbative method itself.

The aim of this paper is on the one hand to benchmark the periodic LMP2 method on a set of molecular crystals, having different size and crystal packing, which are feasible quite straightforwardly and with the need of moderate computational resources. On the other hand, we want to show the many possibilities opened by the local approach,

which allows to easily obtain a deeper understanding of the intermolecular interactions in these systems. Results are reported for the cohesive energy of a set of five molecular crystals including hydrogen bonded (*i.e.* H₂O, NH₃, HCOOH) and dispersion bonded (*i.e.* CO₂, Acetylene) crystals. Formic acid is particularly interesting system, due to its peculiar crystalline structure (see section 3), and has been used by several groups to benchmark electronic structure methods.^{10,33} A systematic comparison with available experimental data is carried out to assess the accuracy of the computed cohesive energies. Since Gaussian-type basis sets were used in the present work, an attention has been paid to the role of the basis set superposition error (BSSE). To complete the discussion, we have analyzed the effect of the recently introduced semi-empirical scaling of the MP2 components (Spin Component Scaling, SCS³⁴), which have recently raised a considerable attention.^{35,36}

Post-HF correlation methods are often used as a benchmark for the tuning of faster but less reliable or less general techniques. In this respect we also compare the LMP2 results with DFT results augmented with an empirical $-f(R)C_6/R^6$ correction to DFT methods recently proposed^{37,38} for molecular systems.

The paper is structured as follows: in section 2.1 a brief overview of the studied systems is reported, while in section 2.2 the details and parameters of the different computational methods are outlined. Section 3 is devoted to the presentation and discussion of the results, first (section 3.1) comparing cohesive energies obtained with different approaches (LMP2, SCS-LMP2, B3LYP-D*), and then analyzing in finer detail the information provided by the LMP2 approach (section 3.2), in particular its long-range contribution (section 3.3).

2 Models and Method

2.1 Systems studied

As briefly outlined in the introduction, the set of systems we have chosen contains crystals more or less dominated by hydrogen bonding (H₂O, NH₃, Formic acid), or dispersive interactions (CO₂, C₂H₂). Formic acid can actually be considered as a “mixed”

system: according to the crystallographic direction chosen, chains of hydrogen-bonded molecules can be found, while the inter-chain or inter-plane binding is due to dispersive interactions (see figure 3). Some information about the systems is reported in table 1.

All the geometries considered in this work are obtained at the experimental lattice parameter, with internal coordinates fully optimized at the B3LYP/6-31G(d,p) level. Details on the optimizations can be found in Ref. 7. Such a strategy for the choice of the equilibrium geometry has been adopted since our LMP2 code does not yet contain an automatic geometry optimizer.

2.2 The LMP2 Method

For a detailed description of theory, algorithms, computational scheme, and capabilities of CRYSCOR we refer to our previous papers.^{20,22–24,31,39} Here we just recall its main features. As mentioned in the introduction, to represent the occupied HF manifold CRYSCOR uses Wannier functions (WF) generated by CRYSTAL;⁴⁰ these are well-localized, symmetry-adapted, mutually orthogonal, translationally repeated functions. Conventionally, only correlations between the valence electrons are considered according to the commonly used “frozen core” approximation. The virtual manifold is described by the nonorthogonal set of projected atomic orbitals (PAOs), obtained by projecting individual AOs out from the occupied subspace. Translational and point symmetry are fully exploited by the codes at all levels. Parameters for the HF calculations are as described in our previous work,³¹ with CRYSTAL tolerances ITOL1-3 set to 7 and ITOL4-5 set to 15 and 50, respectively.

The total LMP2 energy E^{LMP2} can be written as a sum of pair energies E_{ij}^{LMP2} , each corresponding to 2-electron excitations from the given ij -pair of WFs. Translational symmetry allows us to impose the first WF (i) to belong to the reference unit cell. For a given ij -pair the local-correlation Ansatz restricts the virtual space, allowing excitations only to the PAOs in the pair-domain, *i.e.* those, spatially close to at least one of the WFs in the pair. This leads to the linear scaling of the LMP2 method with cell size. In the present work the local excitation domains have been restricted to the molecular units, to which the corresponding Wannier functions belong.

The computational setup used in this work is the one carefully tuned on CO₂ and NH₃ crystals.³¹ The basis set used is the p-aug-TZVPP, that is Ahlrichs' triple-zeta quality set^{41,42} with a double set of polarization functions, augmented with diffuse polarization functions (d- and f- for C, N and O atoms, p- and d- for H atoms) from the correlation-consistent aug-cc-pVTZ by Dunning.^{43,44} The dual basis set technique⁴⁵ has been used in all the calculations. This technique implies evaluation the HF reference with a smaller basis, while the subsequent calculation of the LMP2 correlation energy employs the virtual space represented in a larger basis. The correction to the HF energy is evaluated using the contribution of first-order singles in the larger basis.^{20,32} Such a scheme allowed us to introduce diffuse polarization functions, which are vital for an accurate description of the weak binding, but would normally cause linear dependency and/or numerical instability problems in the HF calculation. In the case of formic acid also the most diffuse d function (p for H atoms) of the TZPP set have been introduced via this technique. One has to be careful, though, since in order to ensure the reliability of the perturbative approach to the singles contribution, the two basis sets should not differ too much, or alternatively the HF energy with the smaller basis should be reasonably close to the basis set limit.

The larger calculation, that is Formic Acid, has been possible thanks to the newly developed parallel version of CRYSCOR,⁴⁶ which allows to distribute the computational burden onto several machines. To quantify the cost of a typical calculation, on an intel Xeon 64 bit machine, the LMP2 part of the simplest calculations (NH₃, CO₂) requires approximately 2 days on a single processor, while the most demanding (Formic Acid) lasted 3 days running on 4 CPUs

2.3 The Spin Component Scaling

In recent years much attention has been raised by the proposal by Grimme,³⁴ to correct some well known bad behavior of the MP2 method by scaling the *singlet* and *triplet* spin components of the MP2 energy, which are equally balanced in the conventional formulation. As clearly exposed by Grimme, the Spin Component Scaling (SCS) approach by no means can be regarded as an *ab initio* wavefunction method, yet

it holds several of the nice features of MP2, like size consistency, and is invariant to unitary transformations within the occupied and virtual orbitals, thus being applicable to Local-MP2 methods. Despite the success the SCS approach for some systems^{47,48} and recent attempts⁴⁹ to shed some light on the fundamental reasons for this somewhat surprising improvement of the results, still the predictive power of these scheme is unclear.

A number of similar scaling schemes with different values for the two factors followed the original Grimme's proposal. Some of these methods consider only the triplet term (Same Spin Scaling, SSS), or conversely only the singlet term (Spin Opposite Scaling, SOS) alone. Head-Gordon and coworkers³⁵ have shown that the previously used scaling factors generally fail to correctly describe intermolecular interactions, proposing a further reparametrized values for the scaling factors: SCS(MI), SOS(MI), and SSS(MI) schemes. Having no intention to clarify this situation, in section 3.1 we show how the SCS and SCS(MI) affect the results of our LMP2 periodic calculations.

Here, we propose a new and simple way of scaling the spin components for molecular crystals, based on a separation between intra- and inter-molecular contributions. It has been suggested in ref. 35, that SCS original scaling factors are good for covalent bonds and intramolecular interactions, while reverse factors have to be used to describe the interactions between molecules. Within the local method we can discriminate between the contributions to the LMP2 energy coming from intra-molecular and inter-molecular WF pairs. Thus the Grimme's original scaling factors can be applied to the short range interactions, while leaving the contributions unscaled for the mid- and long-range contributions to the energy. We refer to this scaling scheme as Mol-SCS, since the scaling applies only to WF pairs within the same molecule. It is conceptually similar to the MOS method⁵⁰ but is very easy to implement and does not introduce new parameters.

2.4 The D* empirical dispersion term for B3LYP

Our LMP2 results are also compared with those obtained with a completely different, semi-empirical approach recently introduced in CRYSTAL.⁷ This approach, called

B3LYP-D*, uses a damped pairwise empirical potential^{37,38} of the form $-f(R)C_6/R^6$ to include long-range dispersion contributions to the computed DFT total energy and gradients at the B3LYP level of theory:

$$E_{B3LYP-D^*} = E_{B3LYP} + E_{D^*} . \quad (1)$$

Empirical parameters, (*i.e.* Van der Waals radii and atomic C_6 coefficients) were taken from Table 1 of Ref. 38. The original Grimme model has been modified by rescaling Van der Waals radii in the damping function, instead of the whole contribution, thus yielding the D* empirical term specifically tuned for molecular crystals. The proposed scaling factors were determined from a manual procedure trying to find the best agreement between computed and experimental cohesive energies on a set of 14 molecular crystals including all those studied in this work but Ice. For more details see ref. 7.

3 Results and Discussion

3.1 Cohesive Energies

Table 2 compiles the computed cohesive energy for the studied molecular crystals obtained with the different methods.

The cohesive energy E_{coh} is given by the expression:

$$E_{coh} = E_{bulk}/Z - E_{mol}^{[gas]} , \quad (2)$$

where Z is the number of molecular units in the unit cell (reported in table 1), and E_{bulk} and $E_{mol}^{[gas]}$ are the total LMP2 energies of the bulk system (per cell) and the molecule in the gas-phase geometry, respectively.

Since finite basis sets are used in the calculations, the basis set superposition error (BSSE) might generate artificial binding due to the inconsistency between the bases in the molecular and bulk calculations. The standard standard Boys-Bernardi counterpoise method⁵¹ has been used, at all levels (HF, LMP2, B3LYP-D*).

In all the studied cases the BSSE correction is quite small, that is about 7-10% of the uncorrected cohesive energy. Computed cohesive energies were compared with lattice energies estimated from experimental sublimation energies⁵² by adding a constant contribution of $2RT$ ⁵³ (i.e. $-\Delta E = \Delta H_{sub}^0(T) + 2RT$) to approximate the zero-point energy and thermal corrections to 298 K. From our experience this simple way of taking into account the thermodynamical corrections to the interaction energy in many cases provides a reasonable estimate. However we point out that within the scale of the relatively small interaction energies, the roughness of this approach, can hinder a firm assignment of the theoretical and experimental data. We can quantify the error bar on the experimental cohesive energies in ± 4 kJ/mol.⁷

From table 2 it is seen that the LMP2 method performs well, in all cases providing a good agreement with the experimental results, with cohesive energies being systematically underestimated. The largest absolute error is seen in the case of Carbon dioxide crystal; we have already shown that this behavior is due to a critical basis set dependence.³¹ Probably the same basis set effect is behind the missing 3 kJ/mol in the binding of C_2H_2 . Other errors in the cohesive energy can be generally attributed to the deficiencies of the LMP2 method itself.

SCS with original scaling factors generally performs more poorly with respect to LMP2 results. Interestingly, for NH_3 , H_2O and Formic acid this result is clearly in line with calculations on molecular dimers.^{35,48} In all cases SCS(MI) gives better cohesive energies than LMP2, or at least not worse. This also agrees with results for molecular dimers. It appears that the behavior of SCS-methods in crystals is rather similar to the molecular dimer case, and thus no further specific reparametrization of the scaling factors should be required for the periodic calculations. Comparing LMP2 and the proposed Mol-SCS, the latter is on average closer to the experimental estimate, improving the result of the most critical systems, like carbon dioxide and formic acid. Overall, LMP2 SCS(MI) and Mol-SCS give results rather similar to each other, with deviations from experiment well within the error bar of the estimated experimental cohesive energies. In any case, they are significantly better than the original SCS scheme.

Considering the B3LYP-D* results it can be seen that it is generally not substan-

tially worse than LMP2, which is although not surprising, since the parametrization of the empirical correction D^* involved these same systems. However for the Acetylene and CO_2 crystals, where the dispersive interaction is the dominant source of binding, the LMP2 is clearly outperforming B3LYP- D^* . In those systems where hydrogen bonding is dominating, B3LYP- D^* generally performs better, but so does also the LMP2 and the results of the two in such cases are comparable. The ability of the B3LYP- D^* scheme to treat H-bonded systems relatively accurately also allows it to provide a good result for Ice XI, which in fact has not been included in the original set for the D^* parametrization.

3.2 Partition of the LMP2 energy

As discussed in section 2.2, the LMP2 energy can be decomposed as a sum of *pair energies*, that is a sum of contributions from each pair of localized orbitals. This allows for a separation of contributions to E_{coh}^{CP} coming from two orbitals located on the same molecule (*intra*-molecular energy) or on two different molecules (*inter*-molecular energy).^{54,55} The first can be compared to the energy of the isolated molecule: this gives us information on how much the single molecule is *destabilized* in terms of its electronic correlation, as a consequence of the crystalline packing. The second contribution describes the correlation between electrons, belonging to different molecular units within the crystal. It is always attractive and forms the driving force for the Van der Waals binding. In figure 1 we have reported the two contributions to the correlation part of cohesive energy of studied compounds. It is shown that the absolute magnitudes of these contributions are considerably large. Part of the repulsive effect observed is due to structural effects, connected to the deformation of the molecule in the bulk with respect to the gas phase geometry. This contribution is very small at the LMP2 level and is reported in figure for the sake of completeness.

Let us consider the particular case of Formic Acid in more detail. The crystalline structure of this bulk crystal, depicted in fig. 3 is made by infinite hydrogen-bonded chains that mutually interact through dipole-dipole and weak dispersive forces. By partitioning these LMP2 contributions, we are able to distinguish in our calculation

the intra-chain from the inter-chain binding contribution: the inter-chain contribution is -23.7 kJ/mol, the intra-chain binding thus results in -37.4 kJ/mol. Note that this last value still includes the HF binding energy of the full bulk crystal, that is -22.8 kJ/mol, which cannot be partitioned. It is reasonable to suppose that, at the HF level, the inter-chain contribution is repulsive, as it is at the DFT level.³³ Therefore the mentioned value of -37.4 kJ/mol contains this positive contribution, which translates to a somewhat (a few kJ/mol) higher intra-chain binding. Interestingly, a pure B3LYP calculation gives a cohesive energy of 31.5 kJ/mol, rather close to the estimated intra-chain binding, thus confirming the role of dispersive interactions. The LMP2 can be compared with the formation energy of the chain, obtained by Hirata,¹⁰ who modeled solid Formic acid as a one-dimensional periodic polymer embedded in a field of point charges. The attractive dispersion and the HF-repulsive effects within this model have been hence completely neglected. However, reported result for an MP2/aug-cc-pVTZ quality calculation was 46 kJ/mol, which fits quite well in this picture.

3.3 Long-range LMP2 intermolecular energy

In figure 2 we report the inter-molecular contribution to the binding as a function of the distance between occupied orbitals (that is Wannier functions). This picture provides information on how the long-range effects of the correlation energy and dispersive effects behave in chemically and physically different molecular crystals. In all the studied systems, ranging from a highly hydrogen-bonded (Ice) to a purely dispersively bound (CO₂) solid, the long range effects give a relevant contribution. For Ice XI, the significant portion (90%) of the cohesive energy lies in the mid-range, that is within 4 Å. It has already been shown by one of us³⁹ that this range is also decisive for the relative stability among different phases of Ice. On the other hand, CO₂ crystal appears to have a large portion (~30%) of its cohesive energy lying beyond 4 Å. Taking as a reference 99% of the cohesive energy (marked by a dotted line in figure), we see that this is reached at 7.5 Å by H₂O crystal, while CO₂ reaches it only at 10 Å. Formic acid and NH₃ have an intermediate behavior with respect to the H₂O and CO₂ crystals, while C₂H₂ has a behavior very similar to CO₂, and has not been reported in figure for

clarity.

In a further analysis, the partitioning of the post-HF local correlation energy allows us to directly compare the dispersive contributions to the cohesive energy, evaluated as the LMP2 energy beyond 4 Å, and through the D^* empirical term. Figure 4 shows the comparison between the two approaches. While the choice to consider the LMP2 contribution from 4 Å is arbitrary, and thus the change in this distance can slightly shift the points in this plot to the left or to the right, a correspondence between the two quantities clearly exists. This interesting result opens the possibility to exploit the LMP2 *ab initio* results for parametrizing empirical models. In particular the atomic C_6 parameter employed in the empirical dispersion term might be obtained directly from periodic calculations, rather than on molecular adducts.

4 Conclusions and Prospects

In this work we have shown that the periodic Local-MP2 approach implemented in the CRYSCOR program can be efficiently applied to the study of molecular crystals. The capabilities of this new computational tool have been tested on a small but representative set of systems, and some features made available by the local approach have been exploited for a fine analysis of the binding effects in weakly bound systems.

The post-HF *ab-initio* LMP2 approach implemented in CRYSCOR has been compared to the B3LYP method augmented with an additional empirical dispersion term (D^*). While the latter is easier and cost-effective, mainly due to the faster convergence of the results with respect to the basis set quality, the LMP2 is a full *ab initio* method, which provides robust and consistent results throughout the studied set. It therefore can also be a relatively good benchmark, useful for parametrizing different models, when the experimental data is lacking or not conclusive, or when simple semiempirical methods could fail. Spin Component Scaling of the LMP2 energy allows for an improvement of the results if applied only to intramolecular contributions (Mol-SCS) or with reparametrized factors (SCS(MI)), but not with original scalings. In perspective, a possible continuation of the present work will be the extension of such studies

to other similar systems. In this respect, aromatic compounds (benzene, naphthalene) would be of particular interest, even if it is expected that LMP2 could overestimate the intermolecular interactions. The LMP2 method could be also very effective in the evaluation of the relative stability of different crystalline phases, which is of great interest in the crystalline engineering.

To improve the quality of the CRYSCOR results the possibility to perform a full geometry optimization at the LMP2 level is the next sensible step, and work is in progress in that direction. Parallelization of the code is also in progress, which will allow the program to become a more routinely usable tool for the study of periodic systems. A preliminary parallel version of the code has been already used for some of the calculations presented in this work, which would be not feasible otherwise due to the large amount of computational resources (mainly memory) required.

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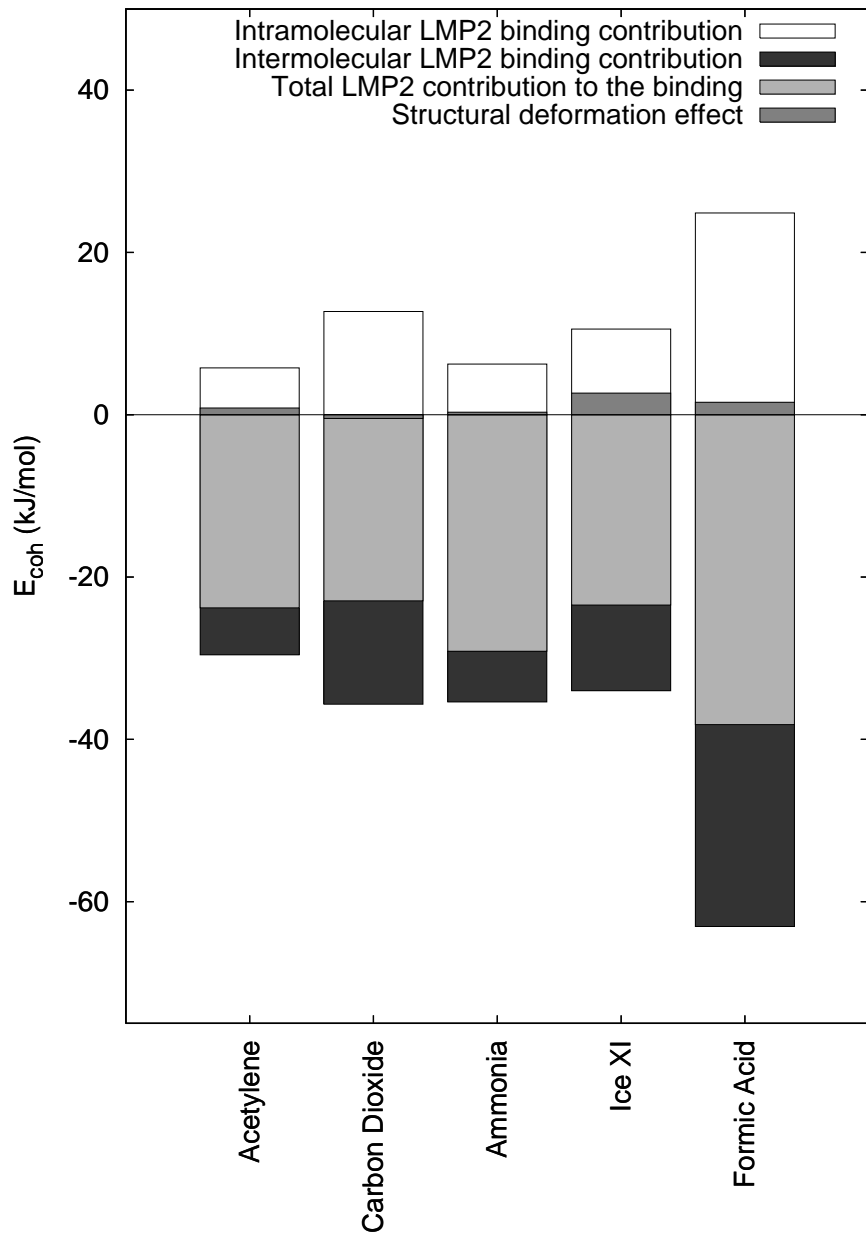


Figure 1: Partition of the LMP2 correlation contribution to the cohesive energy of the studied systems into *inter-* and *intra-* molecular energies. The total correlation contribution is reported, as well as the effect due to deformation of the molecule with respect to the gas phase.

System	Formula	Space Group	n_{mol}^{cell}	n_{ato}^{cell}	$n_{symmops}$
Acetylene	C_2H_2	Pa3	4	16	24
Carbon Dioxide	CO_2	Pa3	4	12	24
Ammonia	NH_3	$P2_13$	4	16	12
Ice XI	H_2O	$Cmc2_1$	4	12	4
Formic Acid	$HCOOH$	$Pna2_1$	4	20	4

Table 1: Information about the systems studied in this work. n_{mol}^{cell} and n_{ato}^{cell} are the number of molecules and the total number of atoms per cell, respectively. $n_{symmops}$ is the number of symmetry operators in the space group.

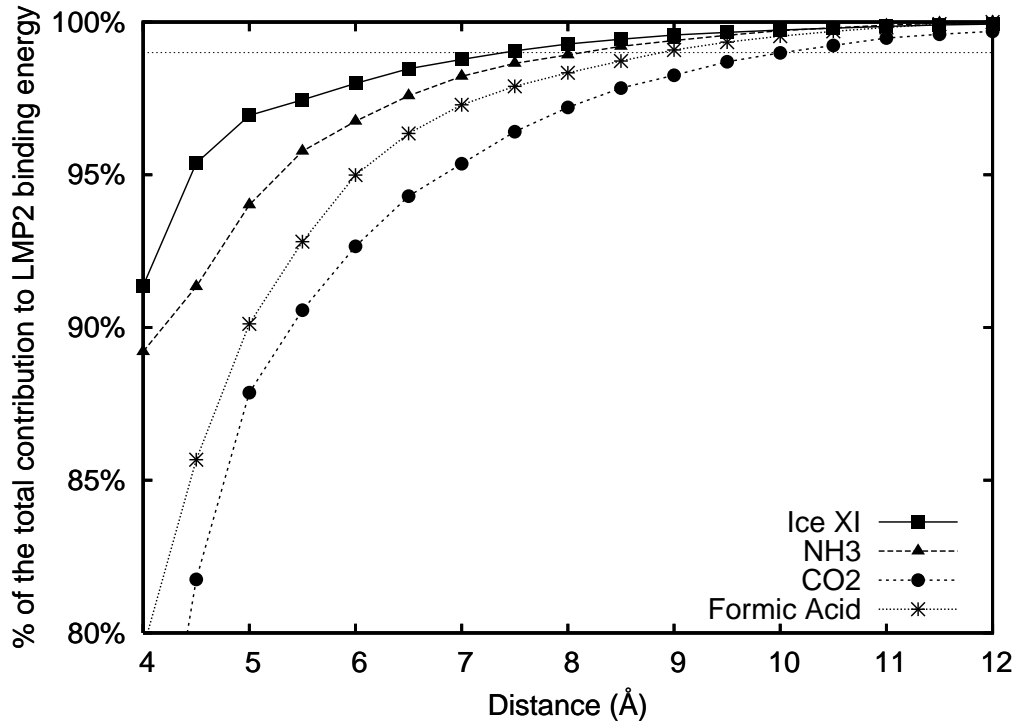


Figure 2: Analysis of the LMP2 correlation contribution, represented as a percentage of the total LMP2 cohesive energy, as a function of the distance between occupied orbitals. A dotted line marks the 99% of the total contribution.

System	LMP2		SCS		SCS(MI)		Mol-SCS		B3LYP-D*		Exp.
	E_{coh}	Δ	E_{coh}	Δ	E_{coh}	Δ	E_{coh}	Δ	E_{coh}	Δ	
Acetylene	-25.7	-2.8	-19.5	-9.0	-26.1	-2.4	-25.7	-2.8	-20.2	-8.3	-28.5
Carbon Dioxide	-25.1	-6.0	-18.4	-12.7	-26.7	-4.4	-26.2	-4.9	-23.1	-8.0	-31.1
Ammonia	-35.3	-1.0	-27.7	-8.6	-35.4	-0.9	-34.8	-1.5	-35.2	-1.1	-36.3
Ice XI	-57.2	-2.0	-50.2	-9.0	-59.0	-0.2	-56.3	-2.9	-60.1	0.9	-59.2
Formic Acid	-61.1	-3.9	-50.4	-14.6	-62.6	-2.4	-63.9	-1.1	-61.3	-3.7	-65.0
MAD ¹		3.1		9.5		2.1		2.6		4.4	
Max ²		-6.0		-14.6		-4.4		-4.9		-8.3	

Table 2: Cohesive energies (in kJ/mol) of the studied systems. p-aug-TZPP basis set has been used for all LMP2 and SCS calculations, while B3LYP-D* results have been obtained with the TZPP basis set. Δ is the deviation from the experimental value.

^aMean Absolute Deviation

^bMaximum error

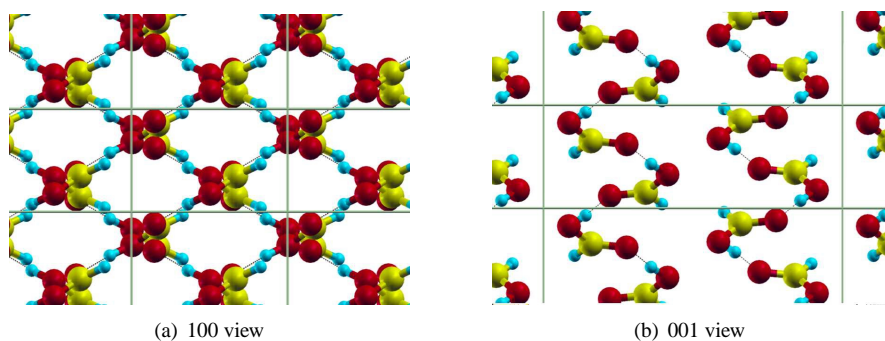


Figure 3: (color online) Two views of the crystalline structure of Formic acid

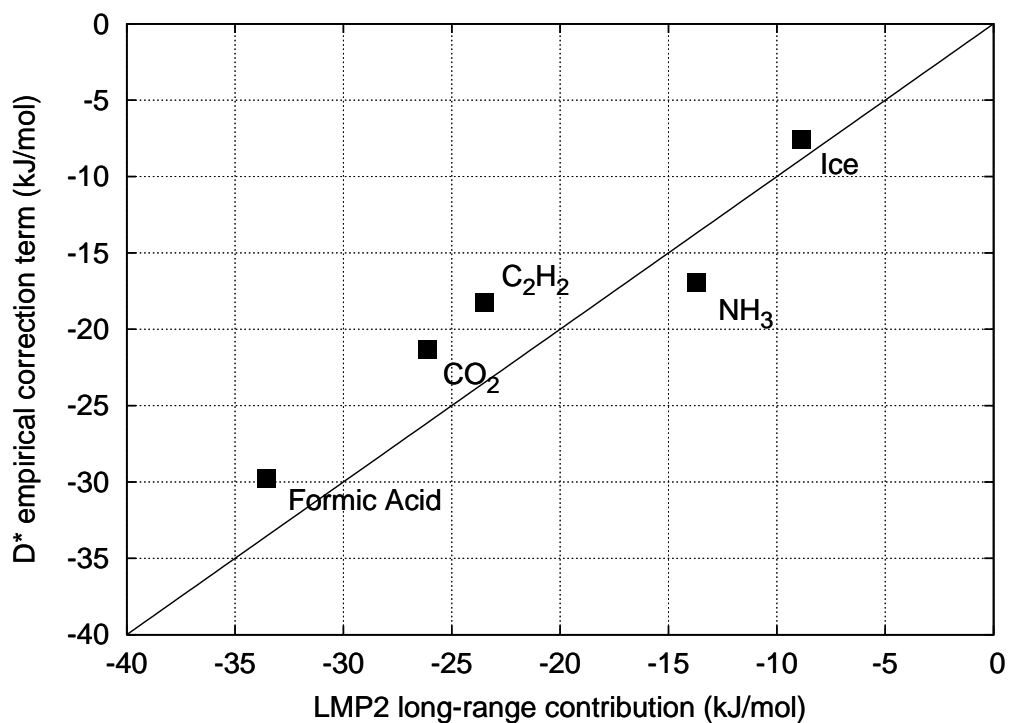


Figure 4: Comparison between the long-range contribution to the binding energy obtained at the LMP2 level as the sum of contributions more distant than 4 Å (x axis) and the D* empirical term (y axis). The y=x line of ideal correlation is drawn as a reference.