

# A periodic Ab initio Quantum Mechanical Calculation of the Vibrational Frequencies of Ammonium Nitrate

\*<sup>1</sup> S. Bourahla, <sup>1</sup>A. Ali Benamara and <sup>2</sup>S. Kouadri Moustefai

<sup>1</sup> Physics Department, Faculty of Science, Laboratory for Theoretical Physics and Materials Physics, Hassiba Benbouali University of Chlef, Chlef, Algeria.

<sup>2</sup> Process Engineering Department, Faculty of Technology, Laboratory of Water and Environment Hassiba Benbouali University of Chlef, Chlef, Algeria.

## Abstract

The structure and vibrational frequencies of ammonium nitrate phases IV and III have been investigated by using the periodic, ab initio program CRYSTAL, which adopts an all-electron Gaussian-type basis set. Hartree-Fock (HF), local density (LDA), gradient-corrected (PW91), and hybrid (B3LYP) density functional have been used. All four different Hamiltonians reproduce the equilibrium geometry of ammonium nitrate phases to good level of accuracy compared to experiments. The obtained structures were used in the prediction of the vibrational frequencies. The effect of basis set and the performance of Hamiltonians, i.e., HF, LDA, PW91, and B3LYP, are discussed, showing that B3LYP performs better than LDA and PW91, which in turn provide better results than HF. The mean absolute deviation from measured frequencies is about 3%, 6% and 6% for B3LYP, PW91 and LDA respectively.

**Key words:** B3LYP, all-electron, ammonium nitrate phases, frequencies, basis set.

## 1. Introduction

Ammonium nitrate AN ( $\text{NH}_4\text{NO}_3$ ) is one of the most important constituents of atmospheric aerosols [1, 2]. Because of their potential environmental impacts, the properties of  $\text{NH}_4\text{NO}_3$  particles have been extensively investigated. From the experimental point of view, infrared (IR) [3-6], Raman [7] spectroscopy and solid state (NMR) spectra [8] has been used to investigate the characteristics of ammonium nitrate. On the theoretical front, first principles calculations using ab initio density functional theory were employed [9, 10] to study proton transfer, electronic properties and low-frequency ( $< 100 \text{ cm}^{-1}$ ) vibrations [11] of ammonium nitrate. To the authors' knowledge, this is the first ab initio work to investigate vibrational frequencies of ammonium nitrate phases in the range  $4000\text{-} 600 \text{ cm}^{-1}$  using CRYSTAL [12], a first-principle, periodic, all-electron computer program that uses a Gaussian-type basis set for representing the electronic crystalline orbitals.

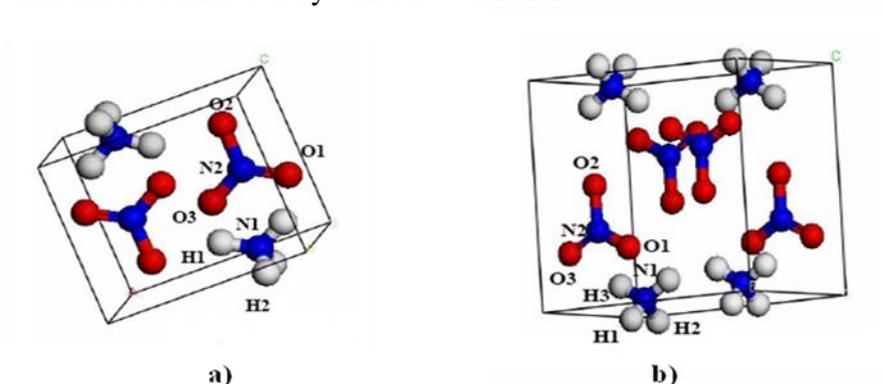
The paper is organized as follows. In section II we summarize the method employed for our calculations. In the Results section, the effect of the basis set and Hamiltonian on the equilibrium geometry and vibrational frequencies are presented and discussed, also in relation to previous determinations. Finally, in the last section, the main conclusions are summarized, and final comments are drawn.

\*Corresponding author: Physics Department, Faculty of Science, Laboratory for Theoretical Physics and Materials Physics, Hassiba Benbouali University of Chlef, Chlef, ALGERIA. E-mail address: bourahlasaida2001@yahoo.fr, Phone: +213559563087.

## 2. Materials and Method

### 2.1. Structural Models

The temperature stability range of AN phase IV is 257-305 K, where its structure has been characterized by X-ray [13] and neutron diffraction studies [14, 15]. This phase belongs to the orthorhombic space group  $Pm\bar{m}n$  and has two  $\text{NH}_4\text{NO}_3$  formula units per unit cell (see Figure 1.a). A two-dimensional infinite network of hydrogen bonds between the N-H atomic pairs of the ammonium group and the O atoms of the nitrate exists in planes parallel to (001) with the adjacent molecular sheets connected by van der Waals forces.



**Figure 1.** Crystal structure of unit cell of ammonium nitrate in phases: a)IV; b)III.

Ammonium nitrate phase III is observed in the temperature range 305-357 K and its structure has been determined by both X-ray [13] and neutron diffraction studies [16]. AV phase III has an orthorhombic unit cell belonging to the  $Pnma$  space group with four  $\text{NH}_4\text{NO}_3$  formula units per unit cell (see Figure 1.b). The hydrogen bonds in this case are much weaker than in phase IV. The weaker hydrogen bonding interactions in phase III allow the existence of large thermal vibrational motions of the ammonium ions leading to the disordered character for this phase.

### 2.2. Theory/calculation

Calculations were performed using the CRYSTAL code [12]. CRYSTAL is a periodic ab initio program, where the crystalline wave functions are expanded as linear combination of atom-centered Gaussian orbitals (LCAO).

Four Hamiltonians have been used: (i) Hartree-Fock (HF); (ii) local density functional (LDA) based on Dirac exchange[17] and the Vosko-Wilk-Nusair [18] correlation contribution; (iii) Perdew-Wang (PW91) gradient corrected exchange and correlation functional [19-22] and (iv) Becke's three-parameter (B3LYP) hybrid exchange functional[23] in combination with the gradient-corrected correlation functional of Lee, Yang, and Parr [24].

Concerning the basis sets, the simplest denoted BS1, contains 21G, 6-21G\* and 6-21G\* for H, O, N, respectively [25, 26], have been used. The exponents of the most diffuse *sp* and *d* orbitals are (0.36, 0.65) for O and (0.28, 0.8) for N. The second basis set BS2 was selected as follows: for oxygen 8-411G basis set as in [27], for nitrogen 6-31d1G basis set as in [28]; and for hydrogen 3-1p1G basis set [28].

The level of accuracy in evaluating the Coulomb and Hartree–Fock exchange series is controlled by five parameters [12], for which standard values have been used (i.e., 6 6 6 6 12). The reciprocal space was sampled according to a regular sublattice with shrinking factor equal to 8. The geometry of these phases, that is inner coordinates, has been optimized within an iterative procedure based on the total energy gradients evaluated analytically [29, 30]. Convergence in the geometry optimization process is tested on the root mean square (RMS), the absolute value of the largest component of both the gradients and the estimated nuclear displacements. The thresholds for the maximum and the RMS forces and the maximum and the RMS atomic displacements on all atoms have been set to (in atomic units) 0.00045, 0.00030 and 0.00180, 0.00120, respectively. About the calculations of vibrational spectra, we refer to previous paper [31] for more explicit formulation of the method. We have performed manipulation and visualization of structures with the MOLDRAW program [32].

### 3. Results

#### 3.1. Geometries

The geometries of the optimized ammonium nitrate phases IV and III were compared to the experimentally determined parameters to assess the quality of the calculations. We report the effects of the basis set on the structural parameters computed with the B3LYP functional together with the experimental geometries [13, 14] for ammonium nitrate phases in table 1.

**Table1.** Effect of the basis set on the structural parameters computed with the B3LYP functional (AN IV, AN III).

Phase	bond lengths(Å)	BS1	BS2	Exp value	bond angles(°)	BS1	BS2	Exp value
AN IV	N2-O1	1.311	1.320	1.274	O1-N2-O2	118.4	122.0	120.0
	N2-O2	1.248	1.279	1.254	O2-N2-O2'	123.1	119.0	120.0
	N1-H1	1.054	1.029	1.069	H1-N1-H1'	111.2	111.9	115.7
	N1-H2	1.056	1.028	1.072	H1-N1-H2	109.5	109.1	109.4
					H2-N1-H2'	109.0	108.9	107.9
AN III	N2-O1	1.261	1.296	1.231	O1-N1-O2	119.9	119.9	119.7
	N2-O2	1.275	1.290	1.275	O2-N1-O2'	120.1	119.9	120.7
	N1-H1	1.047	1.023	1.022	H1-N2-H2	107.6	108.5	101.1
	N1-H2	1.043	1.025	1.041	H1-N2-H3	110.3	111.9	114.9
	N1-H3	1.051	1.028	1.174	H2-N2-H3	109.4	109.2	114.1

Ref [14]: experimental values for AN IV, Ref [13]: experimental values for AN III.

Our results for AN phase IV show that the N-O1 bond length is longer than N-O2 as seen in the literature [9, 14]. The calculated bond angles are estimated by less than 5% for BS1 and BS2 basis sets for the two phases compared to the results presented in [13, 14], excepting the H1-N2-H2 bond angle in the case of AN III phase, which is overestimated by more than 5% for the two basis sets. As a result, bond angles show similar results for BS1 basis set and BS2 basis set for the two ammonium nitrate phases. Regarding bond lengths, the BS1 results are estimated by less than 5%, the same as in the BS2 calculation, excluding some cases. For AN III phase, the bond length N2-O1 are overestimated by about 5% for the BS2, and the N1-H3 bond length was

underestimated by about 10% for the two basis sets. This difference noted in AN phase III case is might due to the fact that the positions of the hydrogen atoms are not known to great accuracy [13]. It can be concluded that the basis set BS1 sufficient to provide an accurate description of these structures. This basis set is used in the calculation of the structural parameters for the four Hamiltonians.

**Table2.** Effect of the functional on the structural parameters (data obtained with the BS1 basis set).

phase	bond lengths	B3LYP	PW91	LDA	HF	Exp value	bond angles	B3LYP	PW91	LDA	HF	Exp value
AN IV	N2-O1	1.311	1.329	1.298	1.259	1.274	O1-N2-O2	118.4	118.2	118.8	118.9	120.0
	N2-O2	1.248	1.261	1.254	1.214	1.254	O2-N2-O2'	123.1	123.5	122.3	122.0	120.0
	N1-H1	1.054	1.060	1.067	1.029	1.069	H1-N1-H1'	111.2	111.3	112	110.9	115.7
	N1-H2	1.056	1.064	1.077	1.031	1.072	H1-N1-H2	109.5	110.3	109.6	109.2	109.4
							H2-N1-H2'	109.0	108.8	106.2	108.9	107.9
AN III	N2-O1	1.261	1.286	1.257	1.224	1.231	O1-N1-O2	119.9	118.5	119.9	120	119.7
	N2-O2	1.275	1.286	1.270	1.232	1.275	O2-N1-O2'	120.1	120.7	119.9	120.1	120.7
	N1-H1	1.047	1.051	1.078	1.030	1.022	H1-N2-H2	107.6	107.2	108.2	107.8	101.1
	N1-H2	1.043	1.059	1.064	1.025	1.041	H1-N2-H3	110.3	112.4	112.2	109.8	114.9
	N1-H3	1.051	1.061	1.057	1.026	1.174	H2-N2-H3	109.4	109.2	109.0	109.6	114.1

Ref [14]: experimental values for AN IV, Ref [13]: experimental values for AN III.

Table 2 shows the equilibrium structural parameters obtained with the adopted Hamiltonians, (i.e., HF, LDA, PW91 and B3LYP) and BS1basis set. All Hamiltonians obtained bond angles agree with to the experimentally results [13, 14] to a good degree of accuracy, with the exception of H1-N2-H2 bond angle in the case of AN III phase is overestimated by about 6%. All bond lengths are well estimated for AN phase IV with deviations about few percents from the experimental results presented in [9, 14]. This results confirm that AN IV is the most stable phase of ammonium nitrate. For AN III phase, LDA, PW91 and P3LYP overestimate the measured parameters N-O and N-H [13], HF underestimates them. It is worth noting, though, all Hamiltonian underestimate the N1-H3 bond length by more than 10%. The bond lengths are underestimated by HF and overestimated by all DFT Hamiltonians in the two AN phases. In overall, the determined structural parameters by LDA, PW91 and B3LYP functionals differ slightly from the HF results.

### 3.2. Vibrational Frequencies

We begin our analysis by comparing the results obtained at the B3LYP level of theory with the two basis set (BS1 and BS2) to each other and to the experimental data. The results by Wu et al. [3] and Koch et al. [4] have been considered as references. As expected, the vibrational frequencies of all AN phases show that,  $\nu_1(\text{NH}_4^+)$ ,  $\nu_2(\text{NH}_4^+)$  are infrared activated modes, which are forbidden in the infrared spectrum for the ammonium isolated ion (see Table 3, 4 ). As well,  $\nu_1(\text{NO}_3^-)$  is forbidden to appear in the infrared spectrum for the nitrate isolated ion, conversely it is an infrared active mode in AN phases.

Table 3 shows that, for AN phase IV , the difference between the results obtained with BS1 and BS2 is about a few percent. The agreement is generally good for all modes, with differences

between calculated and experimental frequencies [3, 4] smaller than 5%. However, 3 modes, in which the difference is +9% for  $\nu_4(\text{NH}_4^+)$  in the case of BS2, +5.7% and +7.5% for  $\nu_2(\text{NO}_3^-)$  in the cases of BS1 and BS2, respectively.

**Table 3.** Effect of the basis set on the vibrational frequencies ( $\text{cm}^{-1}$ ) computed with the B3LYP functional (AN IV).

Vibrational mode	BS1	BS2	Exp value
asymmetric stretching mode $\nu_3(\text{NH}_4^+)$	3278, 3243	3426, 3425	3254 <sup>a</sup>
symmetric stretching mode $\nu_1(\text{NH}_4^+)$	3209	3248	3087 <sup>a</sup>
symmetric deformation mode $\nu_2(\text{NH}_4^+)$	1751	1809	1771 <sup>a</sup>
symmetric deformation mode $\nu_4(\text{NH}_4^+)$	1514	1613	1479 <sup>a</sup>
asymmetric stretching mode $\nu_3(\text{NO}_3^-)$	1324	1384	1350 <sup>a</sup>
symmetric stretching mode $\nu_1(\text{NO}_3^-)$	1059	1071	1051 <sup>a</sup> , (1047, 1041) <sup>b</sup>
out of plane deformation mode $\nu_2(\text{NO}_3^-)$	881	896	833 <sup>a</sup> , (831, 826) <sup>b</sup>
in plane deformation mode $\nu_4(\text{NO}_3^-)$	733	743	716 <sup>b</sup>

<sup>a)</sup> Ref [4], <sup>b)</sup> Ref [3].

**Table 4.** Effect of the basis set on the vibrational frequencies ( $\text{cm}^{-1}$ ) computed with the B3LYP functional (AN III).

Vibrational mode	BS1	BS2	Exp value <sup>b)</sup>
asymmetric stretching mode $\nu_3(\text{NH}_4^+)$	3322	3486	2800-3300
symmetric stretching mode $\nu_1(\text{NH}_4^+)$	3261, 3205	3430, 3229	2800-3300
symmetric deformation mode $\nu_2(\text{NH}_4^+)$	1798	1826	
symmetric deformation mode $\nu_4(\text{NH}_4^+)$	1652	1781	
asymmetric stretching mode $\nu_3(\text{NO}_3^-)$	1525, 1494, 1469	1642, 1346, 1304	1300-1500
symmetric stretching mode $\nu_1(\text{NO}_3^-)$	1095	926	1047
out of plane deformation mode $\nu_2(\text{NO}_3^-)$	890	853	831, 826
in plane deformation mode $\nu_4(\text{NO}_3^-)$	737	735	717

<sup>b)</sup> Ref [3].

Regarding AN phase III (see Table 4), the frequencies obtained with the two basis sets show the same trend as in AN phase IV. The deviation between our results and experiment [3] is less than 5% excluding  $\nu_1(\text{NO}_3^-)$  and  $\nu_3(\text{NH}_4^+)$  for BS2,  $\nu_2(\text{NO}_3^-)$  for BS1, where the differences are in the range 5% - 11%. A possible explanation for these differences between our predicted and experimental vibrational frequencies values can be due to the different temperatures of at which the measurements have been done which they are not considered in our ab initio calculations. Overall, these results indicate that the BS1 basis set is sufficient to predict all frequencies.

Vibrational frequencies in Tables 5 and 6 have been obtained with the four Hamiltonians and the BS1 basis set for the three phases of ammonium nitrate and compared to the experimental data [3, 4].

**Table 5.** Vibrational frequencies ( $\text{cm}^{-1}$ ) computed with the BS1 basis set (AN IV).

Vibrational mode	B3LYP	PW91	LDA	HF	Exp value
asymmetric stretching mode $\nu_3(\text{NH}_4^+)$	3278,3243	3121,3094	3045,3033	3752,3739	3254 <sup>a</sup>
symmetric stretching mode $\nu_1(\text{NH}_4^+)$	3209	3050	2921	3709	3087 <sup>a</sup>
symmetric deformation mode $\nu_2(\text{NH}_4^+)$	1751	1672	1551	2050	1771 <sup>a</sup>
symmetric deformation mode $\nu_4(\text{NH}_4^+)$	1514	1394	1432	1740	1479 <sup>a</sup>
asymmetric stretching mode $\nu_3(\text{NO}_3^-)$	1324	1161	1211	1689	1350 <sup>a</sup>
symmetric stretching mode $\nu_1(\text{NO}_3^-)$	1059	931	991	1324	1051 <sup>a</sup> , (1047, 1041) <sup>b</sup>
out of plane deformation mode $\nu_2(\text{NO}_3^-)$	881	740	763	1286	833 <sup>a</sup> , (831, 826) <sup>b</sup>
in plane deformation mode $\nu_4(\text{NO}_3^-)$	733	650	680	1041	716 <sup>b</sup>

<sup>a)</sup> Ref [4], <sup>b)</sup> Ref [3].

**Table 6.** Vibrational frequencies ( $\text{cm}^{-1}$ ) computed with the BS1 basis set (AN III).

Vibrational mode	B3LYP	PW91	LDA	HF	Exp value <sup>b)</sup>
asymmetric stretching mode $\nu_3(\text{NH}_4^+)$	3322	3233	3191	3782	2800-3300
symmetric stretching mode $\nu_1(\text{NH}_4^+)$	3261,3205	3118,3085	3075,2885	3769,3716	2800-3300
symmetric deformation mode $\nu_2(\text{NH}_4^+)$	1798	1677	1597	2015	
symmetric deformation mode $\nu_4(\text{NH}_4^+)$	1652	1620	1497	1945	
asymmetric stretching mode $\nu_3(\text{NO}_3^-)$	1525,1494,1469	1419,1337,1276	1384,1372,1295	1715,1694,1677	1300-1500
symmetric stretching mode $\nu_1(\text{NO}_3^-)$	1095	981	755	1329	1047
out of plane deformation mode $\nu_2(\text{NO}_3^-)$	890	698	700	1301	831,826
in plane deformation mode $\nu_4(\text{NO}_3^-)$	737	648	670	1038	717

<sup>b)</sup> Ref [3].

In the case of AN IV, the mean absolute deviation from experiment [3, 4] is about 3% for B3LYP with the exception of  $\nu_2(\text{NO}_3^-)$  is overestimated by 6%. The absolute deviation is in the range 1%-10% for PW91 and LDA, excepting some cases ( $\nu_2(\text{NH}_4^+)$ ,  $\nu_3(\text{NO}_3^-)$ ,  $\nu_1(\text{NO}_3^-)$ ,  $\nu_2(\text{NO}_3^-)$ ) where the deviation exceeds 10%, as shown in Table 5. For AN III, the vibrational frequencies are in good agreement with experiment [3], for B3LYP the mean difference is about 3% with the exclusion of  $\nu_2(\text{NO}_3^-)$  is overestimated by 7%. The absolute deviation is in the range 1% - 10% for PW91 and LDA, excluding  $\nu_1(\text{NH}_4^+)$ ,  $\nu_1(\text{NO}_3^-)$ ,  $\nu_2(\text{NO}_3^-)$  which show a large differences more than 10% (see Table 6). On the contrary, the agreement for HF is much worse than with all other Hamiltonian, in all ammonium nitrate phases, the frequencies are overestimated in the case of HF Hamiltonian with very large values.

## Conclusions

The influence of the basis set and the performance of four different Hamiltonians, i.e., HF, LDA, PW91, and B3LYP, on the structural parameters and vibrational frequencies of ammonium nitrate phases IV and III were investigated using a periodic, ab initio approach based on an all-electron Gaussian-type basis set.

A small modified basis set was found to be sufficient to provide a correct description of the structural parameters of these phases. All four functionals reproduced the experimental geometry to a good degree of precision.

The effect of the basis set on the frequencies was computed at the B3LYP level and it was found that the BS1 basis set is sufficient to predict all frequencies. The calculations of the frequencies gave a mean absolute deviation from experiment of 3% for B3LYP; clearly showing that this functional performs extremely well in this case. The mean absolute deviation increased to 6% when PW91 and LDA were used, indicating that B3LYP performs much better than PW91 and LDA, whereas HF is by far the worst approximation of the experimental data. This work confirms the excellent performance of the B3LYP functional in predicting the vibrational frequencies of crystals.

## References

- [1] Seinfeld J H, Pandis S N. Atmospheric chemistry and physics. From air pollution to climate change, New York: Wiley; 1998, p. 441.
- [2] Wexler A S, Seinfeld J. H. The distribution of ammonium salts among a size and composition dispersed aerosol. *Atmos. Environ* 1990; 24:1231–1246.
- [3] Wu H B, Chan M Nin, Chan C K. FTIR Characterization of polymorphic transformation of ammonium nitrate. *Aerosol Sci. Technol.* 2007;41:581–588.
- [4] Koch T G, Holmes N S, Roddis T B, Sodeau J R. Low-temperature photochemistry of submicrometer nitric acid and ammonium nitrate layers *J. Phys. Chem.* 1996; 100:11402–11407.
- [5] Théorêt A, Sandorfy C. Infrared spectra and crystalline phase transitions of ammonium nitrate. *Can. J.Chem.* 1964; 42:57–62.
- [6] Rubasinghege G, Spak S N, Stanier C O, Carmichael G R, Grassian V H. Abiotic mechanism for the formation of atmospheric nitrous oxide from ammonium nitrate *Environ.Sci.Technol.* 2011; 45:2691–2697.
- [7] Kearley G J, Kettle S F A. Solid-state studies. Part XXVII. Raman spectroscopic evidence for heteroionic vibrational coupling in ammonium nitrate III. *J. Phys. Chem.* 1982; 86:4007– 4011.
- [8] Anderson-Altman K L, Grant D M. A solid-state nitrogen-15 NMR study of the phase transitions in ammonium nitrate. *J. Phys. Chem.* 1993; 86:11096–11102.
- [9] Sorescu D C, Thompson D L. Classical and quantum mechanical studies of crystalline ammonium nitrate. *J. Phys. Chem. A.* 2001; 105: 720–733.
- [10] Alavia S, Thompson D L. Theoretical study of proton transfer in ammonium nitrate clusters. *J. Chem. Phys.* 2002; 117:2599–2609.
- [11] Witko E M, Buchanan W D, Korter T M. Terahertz spectroscopy and solid-state density functional theory simulations of the improvised explosive oxidizers potassium nitrate and ammonium nitrate. *J. Phys. Chem. A.* 2011; 115:12410–12418.
- [12] Dovesi R, Saunders, V.R., Roetti, C., Orlando, R., Zicovich-Wilson, C.M., Pascale, F., Civalleri, B., Doll K, Harrison N M, Bush I J, D’Arco Ph, Llunell M.: (2006). CRYSTAL06 User’s manual. University of Torino, Torino. Italy.
- [13] Hoden J R, Dickinson C W. Crystal structures of three solid solution phases of ammonium nitrate and potassium nitrate. *J. Phys. Chem.* 1975; 79:249–256.

- [14] Choi C S, Mapes J E, Prince E. The structure of ammonium nitrate (IV). *Acta Crystallogr.* 1972; B28:1357–1361.
- [15] Choi C S, Prask H. J, Prince E. Phase transitions in ammonium nitrate. *J. Appl. Crystallogr.* 1980; 13:403–409.
- [16] Lucas B. W, Ahtee M, Hewat A W. The structure of phase III ammonium nitrate. *Acta Crystallogr.*, 1980; B36:2005–2009.
- [17] Dirac P A M. Time dependent Hartree-Fock approximation. *Proc. Cambridge Philos. Soc.* 1930; 26:376–385.
- [18] Vosko S H, Wilk L, Nusair M, Accurate spin – dependent electron liquid correlation energies for local spin density calculations: a critical analysis. *Can. J. Phys.* 1980; 58:1200–1210.
- [19] Perdew J P, Wang Y. Accurate and simple density functional for the electronic exchange energy: Generalized gradient approximation. *Phys. Rev. B.* 1986; 33:8800–8802.
- [20] Perdew J P, Wang Y. Erratum: Accurate and simple density functional for the electronic exchange energy: Generalized gradient approximation. *Phys. Rev. B.* 1989; 40:3399–4001.
- [21] Perdew J P. *Electronic Structure of Solids*, Akademie Verlag, Berlin (1991).
- [22] Perdew J P, Wang Y. Accurate and simple analytic representation of the electron gas correlation energy. *Phys. Rev. B.* 1992; 45:13244–13248.
- [23] Becke A D. Density functional thermochemistry. III The role of exact exchange. *J. Chem. Phys.* 1993; 98:5648–5652.
- [24] Lee C, Yang W, Parr R G. Development of the Colle–Salvetti correlation – energy formula into a functional of the electron density. *Phys. Rev. B.* 1988; 37:785–789.
- [25] Binkley J.S, Pople J A, Hehre W.J. Self-consistent molecular orbital methods. 21. Small split-valence basis sets for first-row elements. *J. Am. Chem. Soc.* 1980; 102:939–947.
- [26] Dovesi R, Causa' M, Orlando R, Roetti C. Ab initio approach to molecular crystals: A periodic Hartree-Fock study of crystalline urea. *J. Chem. Phys.* 1990; 92(12):7402–74011.
- [27] Towler M D, Allan N L, Harrison N M, Saunders V R, Mackrodt W C, Aprà E. An ab initio Hartree-Fock study of MnO and NiO. *Phys. Rev.* 1994; B50:5041–5054.
- [28] Gatti M C, Saunders V R, Roetti C. Crystal-field effects on the topological properties of the electron-density in molecular-crystals—the case of urea. *J. Chem. Phys.* 1994; 101:10686 –10696.
- [29] Doll K. Implementation of analytical Hartree-Fock gradients for periodic systems *Comput. Phys. Comm.* 2001; 137:74–88.
- [30] Doll K, Saunders, V R, Harrison, N M. Analytical Hartree-Fock gradients for periodic systems. *Int. J. Quantum. Chem.* 2001; 82:1–13.
- [31] Pascale F, Zicovich–Wilson, C M, López Gejo F, Civalleri B, Orlando R, Dovesi R. The Calculation of the vibrational frequencies of crystalline compounds and its implementation in the CRYSTAL code. *J. Comput. Chem.* 2004; 25:888– 897
- [32] Ugliengo P.: (2006) MOLDRAW. A Program to Display and Manipulate Molecular and Crystal Structures. Torino, <http://www.moldraw.unito.it>.