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An ab initio Hartree–Fock study of electronic and structural properties of MgH_2

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A periodic ab initio Hartree–Fock method has been used to evaluate a number of electronic and structural properties of MgH_2. The calculated quantities are the equilibrium lattice parameters, the cohesive energy, the elastic constants, the energy-band structure, the density of states, the electronic charge distribution and the Compton profiles. For the two former properties correlation effects are taken into account and improve the agreement with the experimental data. The strongly but not fully ionic character of MgH_2 is confirmed by the present study.

1. Introduction

Metal hydrides have long presented – and still present today – considerable interest as a result of their multiple applications [1], in particular as a hydrogen reservoir or for their superconducting properties. Among these compounds, MgH_2 is one of the simplest in terms of its low molecular weigh. It is also one of the most important for the reversible storage of hydrogen because of the high percentage of this element that it can contain. Its potential for utilization is unfortunately diminished to a considerable extent by the weak reaction kinetics of the process:

$$Mg + H_2 = MgH_2 .$$

In order to better understand all the intrinsic properties of the MgH_2 crystal, a number of calculational studies have been conducted over the past several years, following the work of Stander and Pacey [2]. These authors utilized Born–Meyer calculations, considering a compound with a totally ionic character, and which yielded results relatively inconsistent with experimental data. The disagreement was attributed to primarily covalent contributions of bonds in the crystal.

Taking this covalent character into account, Lindner and Berggren [3] with a model similar to that of the free-electron, and Krasko [4] with a perturbational iterative approach [5] both utilized empirical pseudopotentials to deduce the structural and electronic properties of MgH_2. Although the structural parameters (equilibrium lattice parameters, equilibrium cell volume) were in relatively good agreement with experience in both cases, the same was not true for energies. Lindner and Berggren [3] reported that the rutile structure was less stable than the hexagonal structure, whereas Krasko [4] found that binding energy was negative in comparison to the Mg crystal and gaseous H_2.

In an attempt to more fully understand the nature and character of MgH_2 bonds, Yu and Lam [6] recently undertook a detailed study of the electronic and structural properties of this system. The study was based on density functional formalism [7,8], using ab initio core pseudopotentials [9,10], but did not calculate Compton profiles for clarifying the nature of the bonds and for which experimental data are available [11,12].

The aim of the present work was to utilize the Hartree–Fock [HF] ab initio formalism taking all electrons into consideration to propose a thorough ex-

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amination of the structural, dynamic, electronic and diffusional properties of the MgH_2 crystal.

2. Method of calculation

The all electron ab initio self consistent field (SCF) HF-LCAO computational scheme, as implemented in CRYSTAL [13] has been described in previous papers [14–16]. It has recently been applied to simple ionic compounds of magnesium such as MgO [17] and MgF_2 [18] in order to obtain structural, dynamic and electronic properties.

In order to define the reliability of the present data on MgH_2 system we must remember that they are affected by three different kinds of errors. The first is related to the basis set incompleteness, the second to the numerical approximations introduced in the implementation of the HF equations and the third to the "correlation error". To reduce the basis set truncation error to less than 0.5%, 0.2% and 1% for the binding energy the lattice parameters and the elastic constants respectively, a large basis set can be used (see below). As regards the numerical errors introduced in the evaluation of the Coulomb and exchange series, we have adopted values for the computational parameters which control the accuracy of the calculation such that the error bar for binding energy, lattice parameters and elastic constants is about 1 mhartree, 10^{-2} Å and 0.02×10^{12} dyn cm^{-2} respectively. For the so-called "correlation error" the simplest way for taking into account correlation effects is through an a posteriori (after SCF) calculation based on correlation only density functional like formulae applied to the HF charge density. In the present work the Colle–Salvetti [19,20] and Perdew functionals [21,22] are applied only for correcting the binding energy and the structural parameters.

Under ambient conditions MgH_2 crystallizes in the tetragonal phase of the rutile type [23] which has the space group $P_{4_2/mnm}$ with two formula units in the unit cell. The Mg atoms are located at the origin and at the center of the cell. A parameter x describes the position of the four H atoms (fig. 1). This structure has three independent structural and lattice parameters (x, c/a, a) and six independent components of the elasticity tensor.

The basis set adopted for the present calculations

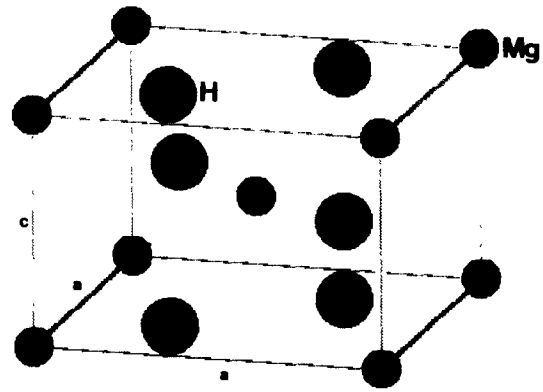

Fig. 1. Arrangement of H and Mg atoms in the tetragonal cell of the rutile type.

is taken from refs. [24,25] respectively for H and Mg. Six and nine atomic orbitals have been used for hydrogen and magnesium from linear combinations of Gaussian type functions (GTF) which are the product of a radial Gaussian times a real solid harmonic function. The two basis sets can be written as 511-1 G and 861 G for H and Mg respectively, where the numbers refer to the level of contraction. For Mg the effect of d functions on the investigated properties has been shown to be negligible.

3. Equilibrium structure and binding energy

The unit cell edges a and c and the hydrogen fractional coordinate x corresponding to the minimum energy at HF level are reported in table 1 and compared with "correlated", experimental [26] and previous theoretical results [3–6]. In order to calculate the equilibrium structural configuration steps of 0.04 Å, 0.03 Å and 0.002 were considered for the three variables a, c and x respectively. At first the cell edges only were changed keeping x fixed at its experimental value, then x was varied separately. Polynomial interpolations yielded the minimum energy results (table 1) corresponding to HF energy −401.57998 au. HF results show quite good agreement with measured data leading the same x value and a c/a ratio within 0.15%. The overestimation of the lattice parameters a and c is 1.2% and 1.4% respectively, giving a unit cell volume of 431.9 au. It should be noted that our unit cell edges results which agree with those

Table 1
Calculated and experimental lattice parameters and binding energy for MgH_2. For lattice parameters, values are given in au (lengths in bohr, volume in bohr^3). For binding energy (BE), values are given in eV. CS means Colle Salvetti's functional. *P* means Perdew's functional

	This work			Exp. [26]	Other calculations		
	HF	CS	*P*		[6]	[3]	[4]
a	8.638	8.423	8.428	8.536	8.604	8.62	8.746
c	5.788			5.709	5.747	6.18	
c/a	0.670			0.669	0.668	0.717	
x	0.306			0.306	0.304	0.306	
cell volume	431.9	400.4	401.1	416	425.5	459.2	447.5
BE	10.88	13.38	12.99	13.4	11.2–13.5		6.4

of Yu and Lam [6] calculated using an ab initio pseudopotential method always overestimate the measured data: this is a well known tendency of the HF calculations.

In order to estimate the effects of the correlation on the lattice parameters calculations were carried out keeping fixed $c/a=0.67$ and $x=0.306$. The two functionals perform nearly in the same way reducing the HF lattice parameters by about 2.5% and giving correlated values lower than the experimental results by about 1% to 1.2% (table 1).

The total crystal energy has been computed for the minimum energy structural parameters at the HF level. The total energy of isolated atoms was evaluated starting from the crystalline basis essentially designed to describe an ionic situation by adding on each center one diffuse sp shell and optimizing exponents of the most diffuse in order to provide additional variational freedom accounting for the tails of the atomic wavefunction. The HF approximation to the binding energy is the difference between crystal and atomic energy i.e. 10.88 eV per unit cell. This result does not include the vibrational energy of the solid. As expected, the HF binding energy is about 19% lower than the experimental value evaluated at 13.4 eV from the heat of formation of the magnesium hydride (0.70 eV/molecule) the cohesive energy of Mg solid (1.52 eV/atom) and the bonding energy of H_2 molecule (4.48 eV/molecule) [27]. The electron correlation correction to binding energy (BE) was estimated as the difference between the correlation energy of the crystal and of the atoms evaluated with the density functional proposed by Colle and Salvetti [19,20] and Perdew [21,22] applied to the HF charge density. It should be noted (table 1) that the absolute correction to BE due to Colle–Salvetti's functional ($\Delta E=2.5$ eV) is 16% higher than that obtained with Perdew 's formula ($\Delta E=2.11$ eV). The difference between our correlated binding energy values (13.38 and 12.99 eV) and the experimental one ranges from 0.02 to 0.41 eV per unit cell. Data calculated by the present method ignore all vibrational contributions to the energy and thus should be compared to the experimental values at 0 K corrected for the effect of zero-point vilbrations.

4. Elastic properties

Elastic constants have been evaluated as second derivative of the total HF crystal energy with respect to the strain components η_i according to a second-order expansion of the elastic energy following:

$$E=\tfrac{1}{2}\sum_{i,j}^{6} C_{ij}\eta_i\eta_j\,.$$

The HF approximation used here, gives usually quite reasonable elastic constants for ionic and semi-ionic systems.

The six elastic constants and the bulk modulus were computed as described in ref. [25] by keeping x and c/a fixed at their equilibrium values. The computed energies E were least-squares fitted to polynomial functions of η up to the third order, yielding the searched $\partial^2E/\partial\eta_i\,\partial\eta_j$ derivatives. Results are listed in

Table 2
Elastic constants (10^{12} dyn cm^{-2}) and bulk modulus (10^{12} dyn cm^{-2}) calculated at Hartree–Fock for MgH_2

	This work	Ref. [6]
$C_{11}+C_{12}$	1.07	1.1
C_{13}	0.22	0.3
C_{33}	1.39	1.0
C_{44}	1.71	
C_{66}	0.22	
B_0	0.49	0.50

table 2 in comparison with those of Yu and Lam [6] only calculated for deformations that do not break the tetragonal symmetry ($C_{11}+C_{12}$, C_{13}, C_{33}) experimental values for C_{ij} being not avalaible for comparison. Concerning the shear elastic constant C_{44} and the C_{66} elastic parameter their determination is new. If for $C_{11}+C_{12}$ our value is in excellent agreement with Yu and Lam's result, a significant discrepancy (about 30%) is observed for C_{33} and C_{13}. The latter can be explained in part to the sum of errors in the linear combination from which it is derived in the two calculations. Due to the compensation effect the difference observed in C_{13} and C_{33} values does not affect the bulk modulus (0.49×10^{12} dyne cm^{-2}) calculated as:

$$B_0=\tfrac{1}{9}[2(C_{11}+C_{12})+4C_{13}+C_{33}]\,.$$

5. Electron band structure. Density of states and charge density. Compton scattering study

The band structure of MgH_2 is computed along the lines (ΓXMΓRAZ, AMXRA) in the first Brillouin zone. An overview of the upper set of the four filled valence band and of the lowest empty conduction bands is shown in fig 2.

The typical features of ionic crystals, small dispersion of valence bands and large gaps appear clearly. The gap width between valence and conduction bands at the Γ point is about 13 eV, against an experimental value of 5.16 eV from an UV-absorption measurement [28] [#1]. The HF approximation is well known to overestimate energy gaps; in this case the error is even larger since the adopted basis set, though quite accurate for representing the ground state, describes the lowest excited state poorly in particular because no diffuse valence orbital on Mg are included. It should be noted that our calculated band gap also differs from the previous calculations performed by Yu

[#1] The results were quoted in ref. [6].

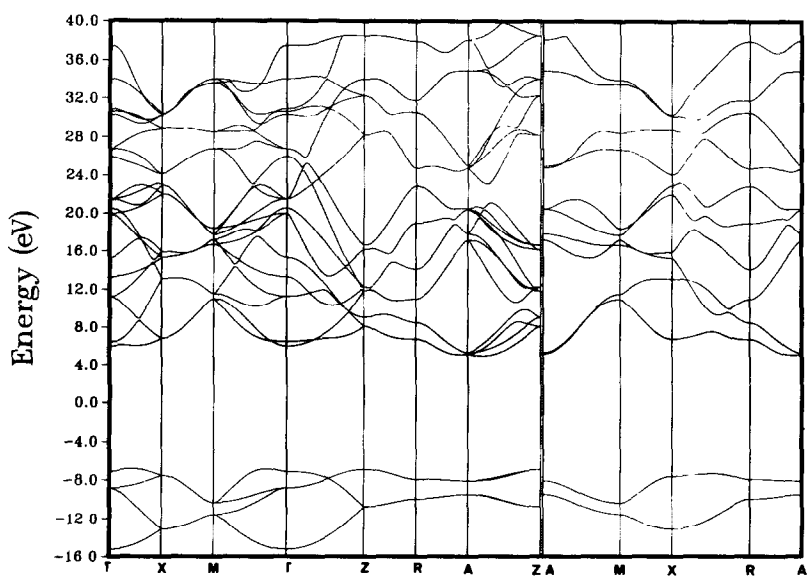

Fig. 2. Electronic energy band structure of MgH_2 plotted along several high symmetry directions.

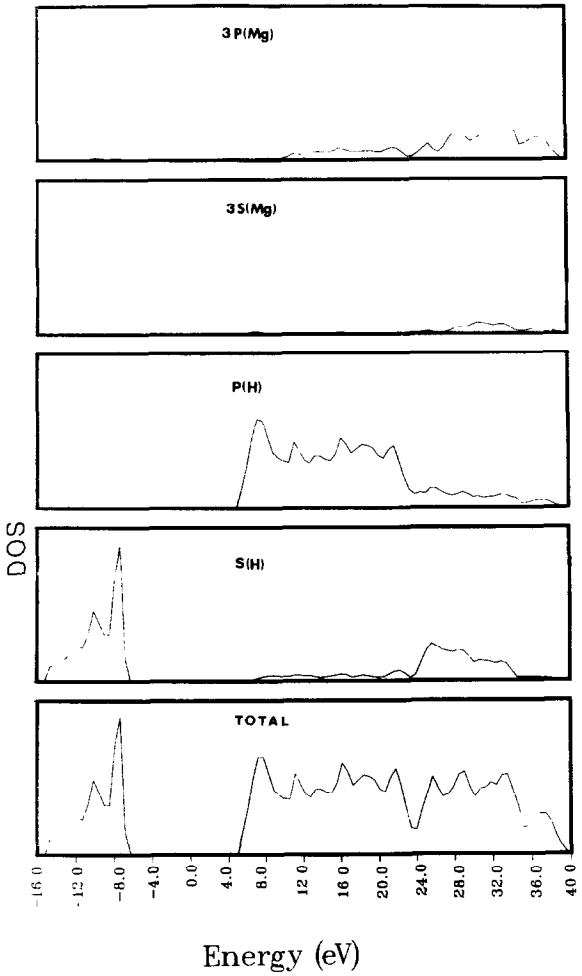

Fig. 3. Total and projected density of states (DOS) of MgH_2. The atomic orbital contributions to the DOS have been obtained using a Mulliken partition scheme.

and Lam [6] (3.06 eV) using a local density approximation known to underestimate the band gap for semiconductors and insulators. In all calculations, the maximum of the valence band is not well distinguished because several maximum energies close to each other within the range of 0.1 eV appear along different symmetry axes.

Inspection of the total and projected densities of electronic states reported in fig. 3 gives a better insight into chemical bonding. The upper part of the valence bands shows that the states are fairly localized on the H atoms. These upper filled bands correspond to nearly pure s orbitals of hydrogen with a small contribution coming from 2p atomic orbitals of magnesium. The main contribution to the lower part of the conduction bands is given by p-type outer orbitals of hydrogen and the influence of 3s and 3p of Mg is practically negligible. In order to verify that this was not related to an effect of the basis set, the exponent of the Gaussian was modified and the basis set of Mg was expanded to 8 5 11. In this way, it was verified that the lowest conduction band were unaffected. A considerable modification was noted only beyond 20 eV. In summary the valence bands of magnesium hydride are determined predominantly by the hydrogen–hydrogen interaction, the cation having a very little influence on the valence band structure.

The degree of ionicity of chemical bonding in MgH_2 can be estimated by results of a Mulliken population analysis. This analysis confirms the ionic nature of chemical bonding in MgH_2: the net charges on Mg ($+1.886|e|$) and H ($-0.943|e|$) are close to the formal ionic value and can be compared with that previously obtained by Krasko [4] and by Yu and Lam [6]. The bond population analysis gives an average positive value of 0.013 e/bohr^3 for the two independent MgH bonds, consistent with the values of atomic charges. It can be noticed that the theoretical results of Krasko [4] and by Yu and Lam [6] seem to provide a picture of Mg–H bond which is less ionic than resulting from the present calculations. Comparable charge values and overlap population are obtained from the same computing method on MgF_2 [25] even though MgO [29] presents a fully ionic behaviour.

The electron charge density has been computed on the (110) and (1$\bar{1}$0) planes emphasizing for the MgH_2 structure the environments of Mg^{2+} and H^-, respectively. Total and difference electron density maps are reported in fig. 4 for the two planes. The difference maps are constructed as total crystal minus ionic superposition densities. As for MgF_2, in both cases the electron clouds of anions and cations appear to contract in the crystal with respect to the free ion references. This contraction due both to electron exchange repulsion and to the compression effect of the crystal electrostatic fields on the electron cloud agrees with results of the breathing shell model [30,31].

Compton scattering is a very accurate test of cal-

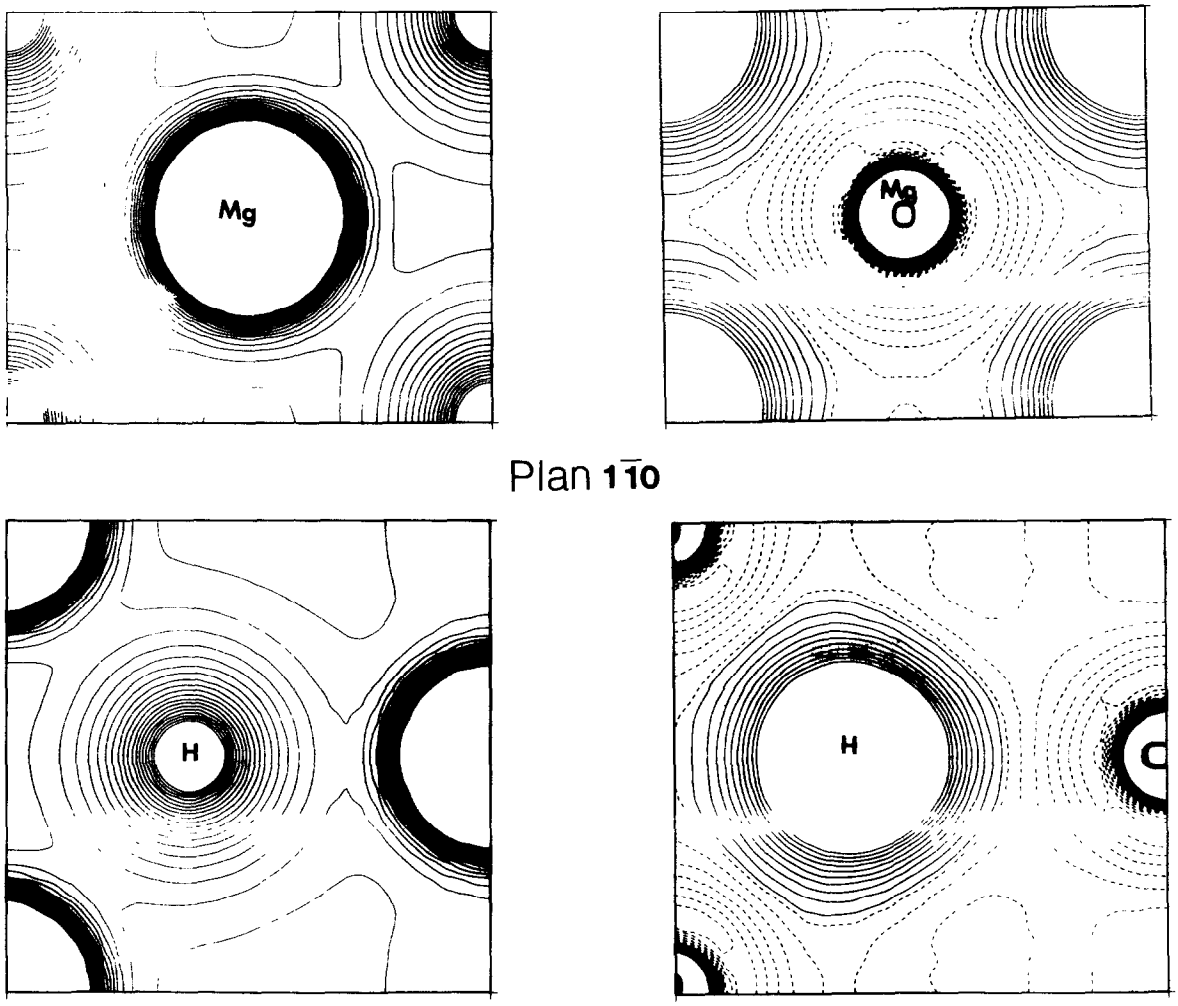

Fig. 4. Total and difference (cristal minus ionic superposition) electron density map on the (110) and (1$\bar{1}$0) planes. Isodensity curves are separated by 0.01 e/bohr^3 and by 0.001 e/bohr^3 for total and difference charge density respectively. Continuous and dashed lines indicate positive and negative values, respectively.

culated wavefunctions. In the present study we have calculated the valence Compton profile of polycrystalline MgH_2 and compared our results with experiments [11,12] and previous theoretical approaches [11,12] by means of the orthogonalized-plane-wave method (OPW) and the LCAO method based on Lowdin's symmetrical orthogonalization of atomic orbitals including large overlaps [11]. The Compton profiles are calculated by numerical integration of the electron momentum density along regularly spaced planes perpendicular to the selected direction; at intermediate points, they are evaluated by interpolation. Interpolated and convoluted valence Compton profile are reported in table 3. Only the convoluted profiles (convoluted in all cases with a resolution width of 0.2 au) can be compared with the experimental data [12]. It is seen that our calculated Compton profile is in better agreement with the experimental profile than the OPW and LCAO results [11]. The major discrepancy between our calculated and the experimental data appears for the small values of q, a satisfactory agreement being found for momentum values larger than 1.0 au. The precision of our calculation for the low energy side until $q = 1.0$

Table 3
Comparison between the experimental valence Compton profile of polycrystalline MgH_2 and convoluted theoretical profile

q (au)	OPW [a]	LCAO [a]	Our work		Exp. [a]
			b)	a)	
0.0	3.048	3.164	3.118	2.927	2.773
0.1	3.010	3.127	3.071	2.883	2.757
0.2	2.897	2.993	2.930	2.753	2.692
0.3	2.710	2.753	2.700	2.542	2.504
0.4	2.450	2.422	2.386	2.264	2.255
0.5	2.125	2.017	2.003	1.937	1.953
0.6	1.740	1.571	1.575	1.587	1.601
0.7	1.321	1.138	1.151	1.242	1.213
0.8	0.910	0.770	0.782	0.929	0.872
0.9	0.563	0.494	0.512	0.668	0.660
1.0	0.327	0.313	0.333	0.465	0.477
1.2	0.114	0.136	0.155	0.218	0.248
1.4	0.031	0.064	0.086	0.109	0.146
1.6	0.005	0.039	0.052	0.062	0.055
1.8	0.000	0.023	0.034	0.038	0.045
2.0	0.000	0.016	0.023	0.025	0.026

[a] Convoluted Compton profile (resolution width of 0.2 au).
[b] Interpolated Compton profile.

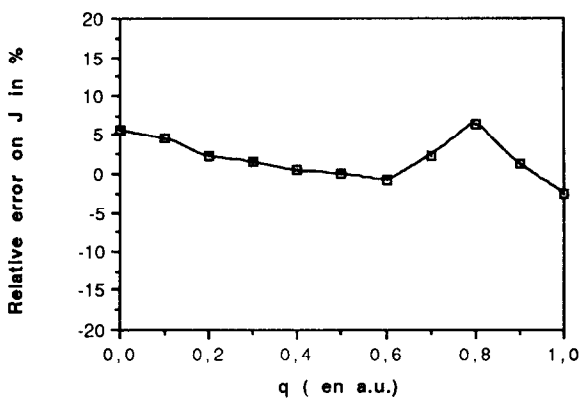

Fig. 5. Relative difference percentage between calculated and experimental valence Compton profile for the low energy side of polycrystalline MgH_2.

au can be seen from fig. 5 where we plot the relative differences between our calculation and experimental data. The most important relative error is not bigger than 6.5% for the value of q equal to 0.8 au.

6. Conclusions

A quite complete ab initio study of crystalline MgH_2 has been presented. The HF results are, in general, in satisfactory agreement with the available experimental data and confirm the essentially ionic structure of MgH_2. The simple a posteriori estimate of correlation effects corrects for the available structural properties as lattice parameters and cohesive energy a part of the HF error and generally brings these calculated data into more satisfactory agreement with experiment.

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