

## ARTICLES

Influence of Electronic Correlation on Structural, Dynamic, and Elastic Properties of Mg<sub>2</sub>Si

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A wide variety of *ab initio* methods are used to study systematically the effects of electronic correlation on the charge density distribution, band structure, lattice parameters, phonon frequencies at the Brillouin zone center, and first-order elastic constants ( $C_{ij}$ ) of Mg<sub>2</sub>Si. Two distinct atom-centered basis sets have been used: an all electron one, and another associated with core pseudopotentials. Various levels of approximation have been tested: (i) HF (Hartree–Fock–Roothaan) calculations with no correlation energy correction; (ii) Hartree–Fock plus a posteriori correlation energy correction estimated using various DFT (density functional theory) correlation functionals applied to the Hartree–Fock electronic density; (iii) DFT calculations with “exact” HF exchange and various DFT correlation functionals; (iv) “complete” DFT calculations in which both exchange and correlation are treated using a selection of exchange–correlation functionals. On the ground of a comparison of the numerous data, complemented by plotted band structure and electronic density maps, the advantages and drawbacks of the representation of correlation within the four levels of approximation are discussed. Special focus is placed on the need for including correlation in the calculation of properties related to derivatives of the electronic potential energy surface of the crystal (phonon frequencies) and to electronically excited states (band gap problem). Because of the peculiar partitions of exchange and correlation energies in DFT functionals, it is emphasized that the combination of HF exchange with DFT correlation functionals is inadequate and may even worsen the HF errors on dynamical quantities involving inner atomic displacements. In contrast, more satisfactory results are generally obtained carrying out complete exchange–correlation calculations.

## 1. Introduction

Electronic correlation is an essential feature for modern quantum calculations in solid-state physics. Many aspects of correlation have been extensively reviewed by Fulde<sup>1</sup> at different levels of approximation and on all kinds of systems from molecules to metals and a wide range of phenomena from molecular dissociation to collective processes such as superconductivity. The present paper is primarily devoted to a quantitative study of the influence of correlation on electronic structure, elastic properties, and harmonic vibrational frequencies. These characteristics are of interest for many areas of physics and chemistry (for instance, vibrational frequencies can serve as tests of stability of the different phases in the problem of phase transitions in the solid-state). Therefore their determination via *ab initio* computational methods and especially a knowledge of correlation effects are of growing importance. The particular case of magnesium silicide Mg<sub>2</sub>Si is chosen as a leading strand for the discussion. Mg<sub>2</sub>Si is a semiconductor that crystallizes in the antifluorite structure with one molecular unit per primitive cell and four formulas per fcc conventional cell (space group *Fm3m*). Its electronic structure, phonon modes, and elastic constants have been previously studied<sup>2</sup> at the Hartree–Fock level using the *ab initio self-consistent field Hartree–Fock linear combination of atomic orbitals* (SCF-HF-LCAO) computational method. However, although the Hartree–Fock Hamiltonian has the advantage of including the exact

exchange energy, it has a well-known deficiency: it ignores electron correlation.

Standard methods employed to add correlation beyond Hartree–Fock calculations in molecular systems, like configuration interaction, are too heavy to be applied in periodic systems. However, computational methods connected with density functional theory, which possesses an approximate expression for the effective exchange–correlation potential, have been applied for many years to crystalline solids using various basis sets such as plane waves<sup>3</sup>, muffin tin orbitals,<sup>4</sup> augmented plane waves<sup>5</sup> and, to a lesser extent, SCF-LCAO.<sup>6,7</sup> In addition to purely Hartree–Fock calculations, the CRYSTAL-95 suite of programs<sup>8</sup> has been designed to include the possibility of carrying out calculations using the density functional theory (DFT) LCAO method. This makes it possible to compare the results of the application of (correlated) DFT and (not correlated) HF methods to condensed matter.

For this purpose, several ways of correcting the Hartree–Fock approximation can be used: one can estimate a posteriori correlation energy using various DFT correlation functionals applied to HF electronic density, one can also carry out DFT calculations combining HF exchange and a DFT correlation functional, and finally one can perform full DFT calculations using various DFT exchange–correlation functionals. This work provides the possibility to compare and discuss, on the case study of Mg<sub>2</sub>Si, the way in which those various manners of

taking correlation into account act in the calculation of selected properties connected to the derivatives of the potential energy surface.

## 2. Methodology

The calculations were performed using the CRYSTAL-95 program<sup>8</sup> quoted in the Introduction. This program provides self-consistent field (SCF) solutions either to the Hartree–Fock–Roothaan (HF) equations or to the Kohn–Sham equations<sup>9,10</sup> (density functional theory (DFT)) subject to periodic boundary conditions with the use of linear combination of atomic orbitals (LCAO). For our purpose, it makes it possible to calculate and compare electronic energies, structures, and related properties both at the HF and DFT levels. This is especially instructive if one keeps constant the computational conditions such as the basis set composition and the level of accuracy on the integrals or sum truncations. Details of the mathematical formulation of the method can be found elsewhere.<sup>11</sup> Essentially, the crystalline orbitals are expanded in the form of Bloch functions, themselves developed on an atomic orbital (AO) basis set. Each AO is a linear combination of Gaussian type functions. The choice of the size and composition of the basis set is a crucial aspect of this type of calculation. Two basis sets were used here: an all-electron basis set (AE\*) and a valence-only basis set (PP\*) associated with Durand–Barthelat pseudopotentials.<sup>12–15</sup> These two sets were optimized with periodic Hartree–Fock calculations and have been described in full details earlier.<sup>2</sup> Each of them was used for both the HF and KS calculations. It was not deemed necessary to re-optimize the basis sets for KS calculations since previous computations have shown that similar behavior of the calculated quantities can be expected when one uses the same basis set in both the HF and KS approximations<sup>16,17</sup> provided this basis set is flexible enough. Moreover, using differently optimized basis sets would have darkened the significance of the planned comparisons.

The Hartree–Fock electron density  $\rho_{\text{HF}}$  and the Kohn–Sham density  $\rho_{\text{KS}}$  (following the notation of Causà and Zupan)<sup>18,19</sup> are defined by the same formula:

$$\rho_{\text{HF/KS}}(\mathbf{r}) = \int_{\text{Brill. Zone}} d\mathbf{k} \sum_{i, \text{occ. bands}[\mathbf{k}]} |\varphi_{i,\text{HF/KS}}^{\mathbf{k}}|^2$$

where  $\rho_{\text{HF/KS}}$  indicates either HF or KS densities.

The crystalline orbitals  $\varphi_{i,\text{HF/KS}}^{\mathbf{k}}(\mathbf{r})$  are solutions of different one-particle equations:

in the Hartree–Fock model

$$\hat{h}_{\text{HF}} \varphi_{i,\text{HF}}^{\mathbf{k}}(\mathbf{r}) = [\hat{t} + \hat{v} + \hat{J}[\rho(\mathbf{r})] + \hat{K}_{\text{HF}}[\rho(\mathbf{r}, \mathbf{r}')] ] \varphi_{i,\text{HF}}^{\mathbf{k}}(\mathbf{r})$$

where  $\hat{t}$ ,  $\hat{v}$ ,  $\hat{J}$  and  $\hat{K}$  are, respectively, the kinetic, the external-potential, the Coulomb, and the (non local) exchange operators. in the Kohn–Sham model

$$\hat{h}_{\text{KS}} \varphi_{i,\text{KS}}^{\mathbf{k}}(\mathbf{r}) = [\hat{t} + \hat{v} + \hat{J}[\rho(\mathbf{r})] + \hat{v}_{\text{xc}}[\rho(\mathbf{r})]] \varphi_{i,\text{KS}}^{\mathbf{k}}(\mathbf{r})$$

The exchange–correlation  $\hat{v}_{\text{xc}}$  is the functional derivative of the exchange–correlation density–functional energy:  $\hat{v}_{\text{xc}}[\rho(\mathbf{r})] = \delta E_{\text{xc}} / \delta \rho(\mathbf{r})$ , where  $E_{\text{xc}} = \int_{\text{unit cell}} d\mathbf{r} \epsilon_{\text{xc}}[\rho(\mathbf{r})]$ .

The main deficiency of the Hartree–Fock approximation is inherent to the one electron model that underlies this method, in which electron correlation is ignored; on the other hand, DFT takes correlation into account, at least most of its dynamic part<sup>20</sup> (the status of static correlation is not well established; at the molecular level, it has been suggested to complete a DFT

calculation by a configuration interaction limited to static effects<sup>21</sup> but this poses fundamental difficulties).

In this work, four types of calculations have been performed to measure the influence of the various ways of taking correlation into account:

(i) Hartree–Fock–Roothaan calculations with no correlation energy correction.<sup>2</sup>

(ii) HF calculations plus a posteriori correlation energy corrections estimated using various DFT correlation functionals applied to the Hartree–Fock electronic density.<sup>18,22–24</sup> The Colle–Salvetti<sup>26,27</sup> (CS), the Lee–Yang–Parr<sup>28</sup> (LYP), and the Perdew Wang generalized gradient approximation<sup>29–31</sup> (PWGGA) correlations functional have been employed.

(iii) DFT calculations with HF “exact” exchange and a DFT correlation functional. As the Hartree–Fock exchange is considered to be the “exact” exchange, it was interesting to combine HF exchange with DFT correlation. For this purpose, a correlation-only Kohn–Sham operator  $\hat{h}_{\text{HF-KS}_{\text{correl}}}$  has been defined:<sup>18,19</sup>

$$\hat{h}_{\text{HF-KS}_{\text{correl}}} = \hat{t} + \hat{v} + \hat{J}[\rho(\mathbf{r})] + \hat{K}_{\text{HF}}[\rho(\mathbf{r}, \mathbf{r}')] + \hat{v}_{\text{c}}[\rho(\mathbf{r})]$$

The LYP, PWGGA, and the Vosko–Wilk–Nusair<sup>32</sup> (VWN for the LDA approximation) correlation functionals have been used.

(iv) “Complete” DFT calculations in which both exchange and correlation have been treated by DFT. The  $\hat{v}_{\text{xc}}$  potential was either the full PWGGA exchange–correlation form,<sup>29,30,31</sup> the combination of the exchange LDA<sup>33</sup> and VWN correlation functionals<sup>32</sup> the BECKE<sup>34</sup> exchange and LYP<sup>28</sup> correlation functionals. In the DFT LCAO method, to facilitate basis set expansion of the one-electron equations,<sup>35</sup> the  $\hat{v}_{\text{xc}}$  potential is fitted by a linear combination of Gaussian-type functions  $G_j(\mathbf{r})$  of an auxiliary basis set:

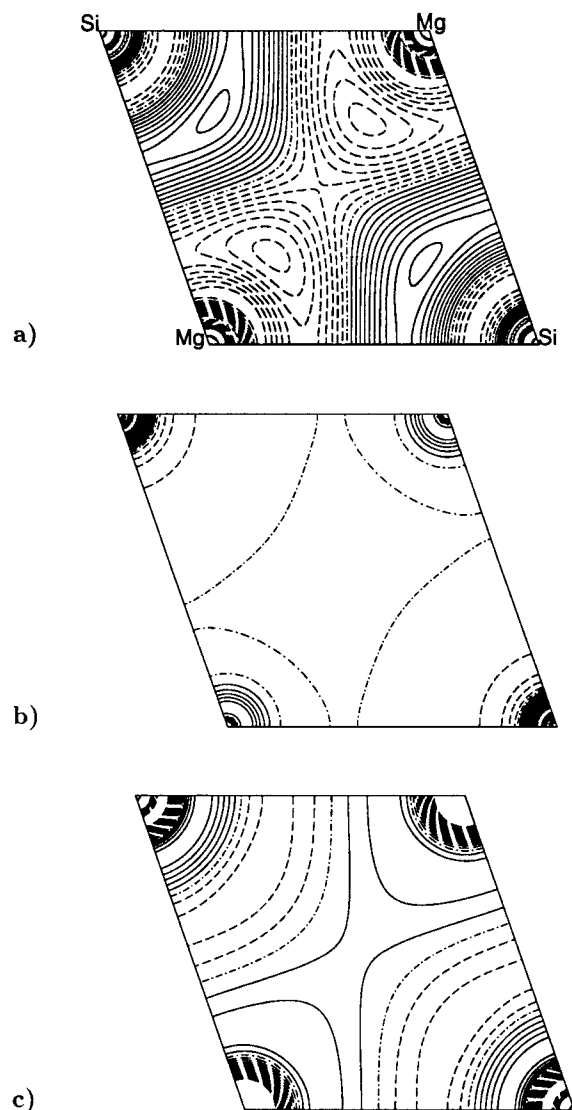
$$\hat{v}_{\text{xc}}(\mathbf{r}) = \sum_j^N c_j G_j(\mathbf{r})$$

This basis set is totally symmetric with respect to translations and rotations, so that it is a basis of the total symmetric irreducible representation of the space group. Such auxiliary basis sets have been introduced by Baerends et al.<sup>36</sup> to treat the problem of the evaluation of the Coulomb potential and extended to the evaluation of the exchange–correlation potential by Dunlap et al.<sup>37,38</sup> In the present work, a set of 12 even-tempered Gaussian functions for each atom has been used: the exponential exponents lie within an interval that ranges from 2000 to 0.1 bohr<sup>−2</sup>. Only fitting functions with *s* angular symmetry have been adopted: *p*, *d*, and *f* functions do not give any contribution to the fitting, due to the cubic symmetry.

## 3. Results and Discussion

The general features of the influence of the electronic correlation on the electronic charge density, on the adiabatic dissociation energy, and on the valence electronic band structure of Mg<sub>2</sub> Si will be discussed with the help of the examples presented in Figures 1 and 2 respectively. The Mulliken population analyses of the charge distribution are reported in Table 1. The values of lattice parameters, elastic constants, and phonon mode frequencies calculated with each of the two basis sets and using methods i–iv to estimate exchange and correlation energies as described above are given in Table 2. These data are discussed in the rest of this chapter.

**A. Electronic Density Maps and Band Structure. 1. Electronic Maps.** In this section, the difference between HF and



**Figure 1.** Comparison between DFT-PWGGA and HF electronic charge distributions (electron density) of  $\text{Mg}_2\text{Si}$  on the (110) plane passing through Mg and Si nuclei. (a) Difference between HF density and overlapping free atom densities, (b) difference between  $\text{AE}^*/\text{xHF-cPWGGA}$  (Hartree-Fock exchange and PWGGA correlation) density and  $\text{AE}^*$  (HF) density, (c) difference between  $\text{AE}^*/\text{xcPWGGA}$  density and  $\text{AE}^*$  (HF) density. Continuous lines correspond to positive values, dotted lines correspond to negative values, dot-dashed lines correspond to zero value. The curves closest to atomic centers correspond to a density of 0.02 atomic units (electron per bohr<sup>-3</sup>). The separation between isodensity curves is 0.001 a.u.

KS densities is discussed. For this purpose, we use the KS density obtained with the Perdew Wang generalized gradient approximation (results obtained with the other functionals exhibit the same behavior). Similar comparative studies were performed, among others, for solids such as silicon<sup>18,18</sup> and for various molecules and atoms.<sup>39</sup>

**1.1.** The difference between the HF density of bulk  $\text{Mg}_2\text{Si}$  and the density obtained by overlapping the Mg and Si free atom densities is presented in Figure 1a. This figure displays the charge transfers that occur in the solid at the HF level. It shows that the nature of the Mg–Si bonding in magnesium silicide is between covalent and ionic<sup>2</sup> (see Table 1). This mixed character may explain the controversy that arose from the interpretation of various experimental data.<sup>40,41</sup> Figure 1a is also helpful as a reference in view of better comparatively appreciat-

ing the extra charge transfers of smaller magnitude due to correlation and presented below in Figure 1b,c.

**1.2.** The PWGGA correlation effects can be analyzed from Figure 1b where the HF density is subtracted from the  $\text{AE}^*/\text{xHF-cPWGGA}$  density resulting from method iii (exact HF exchange and PWGGA correlation). The effect of correlation is to correct the Coulomb hole by confining the electronic charges toward the cores. This is connected with the decrease of the lattice constant (see Table 2). But the structure of the Mg–Si bonding in terms of net charges is little affected:  $\text{Mg}^{0.85+}\text{Si}^{1.7-}$  (to compare with  $\text{Mg}^{0.9+}\text{Si}^{1.8-}$  for HF). However, as discussed later on, it is questionable whether it is adequate to associate an exact Hartree–Fock exchange with a density functional designed for DFT.

**1.3.** Figure 1c shows the difference between the Kohn–Sham density (method iv: full DFT), in the PWGGA approximation, and the HF density. In the neighborhood of the equilibrium geometry, the “ionic” configuration tends to be enhanced at the HF level. In the practical applications of DFT, at the equilibrium geometry, dynamic correlation is usually considered to be fully taken into account.<sup>20</sup> In this case, Figure 1c shows that the form<sup>42</sup> of  $\hat{v}_{\text{xc}}[\rho(\mathbf{r})]$  tends to deplete charge from (HF) high-density regions and to diffuse it toward (HF) low-density regions with some confining of electrons in a region located near the nuclei (effect of the Coulomb correlation). From inspection of the Mulliken population analyses given in Table 1, it is clear that including both exchange and correlation within the framework of the Kohn–Sham (iv) method strongly increases the covalency of the Mg–Si bonding: the KS charge partition is  $\text{Mg}^{0.65+}\text{Si}^{1.3-}$  instead of  $\text{Mg}^{0.9+}\text{Si}^{1.8-}$  at the HF level.

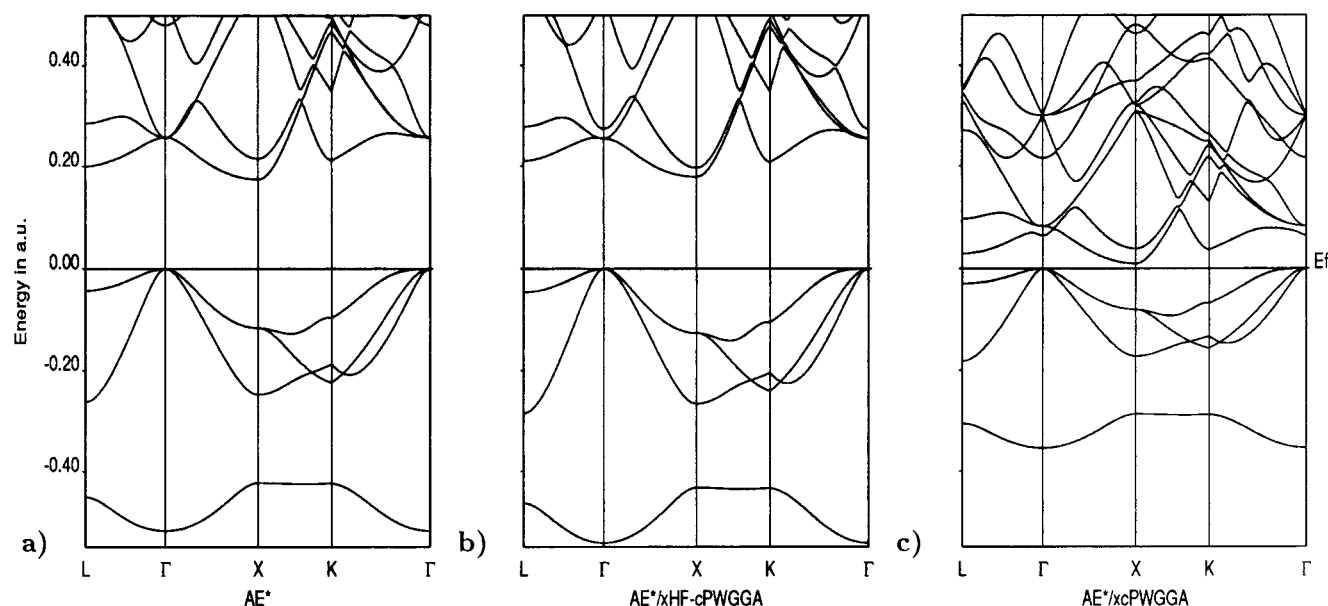
**2. Band Structure.**  $\text{Mg}_2\text{Si}$  is experimentally known to be a semiconductor with a small band gap of 2.27 eV.<sup>43</sup> The various band structures (calculated with the  $\text{AE}^*$  basis set) are drawn in Figure 2. At the HF level (Figure 2a), the band gap between valence and conduction bands at the  $\Gamma$  point is about three times larger than the experimental value. This overestimation reflects a well-known failure of the Hartree–Fock approximation for the properties of band structures, due to a singularity in the exchange contribution to the band energies.<sup>44,45</sup>

Adding a correlation functional to HF exchange (Figure 2b) does not correct this defect. The band gap remains unchanged while the bandwidth is increased  $\approx 8\%$  at the  $\Gamma$  point. Again, this can be thought of as reflecting the fact that the association of a correlation functional to the Hartree–Fock exchange (method iii) is unsatisfactory. This is not really surprising for it has been recognized<sup>42</sup> that the separation between correlation and exchange in the Kohn–Sham scheme depends on the choice of the partition of the exchange–correlation functional and does not fit with the conventional view of the Hartree–Fock theory.

In the Kohn–Sham model, the use of exchange–correlation functionals, which do not suffer from the “exchange pathology”,<sup>45</sup> leads to band separations that are smaller than experimentally found. Thus the band gap at the  $\Gamma$  point decreases to 1.65 eV (to compare to 2.27 eV experimentally). This underestimation is due to the poor description of excited states in which the polarization effect is not accounted for by the usual functionals used in DFT.<sup>1</sup> Städele et al.<sup>46</sup> have attempted to correct this deficiency and they obtained indeed good results by inserting a linear response constant  $\chi_0$  in their own exchange–correlation functional. Anyway, as discussed by Jones and Gunnarson,<sup>47</sup> DFT is known not to have been designed to reproduce accurately the band gap.

**B. Crystal Structure, Elastic Constants, and Phonon Frequencies.**  $\text{Mg}_2\text{Si}$  is known to have a cubic structure so that





**Figure 2.** Valence electronic band structure of  $\text{Mg}_2\text{Si}$  obtained with  $\text{AE}^*$  basis set. (a) HF band structure;<sup>2</sup> (b) xHF-cPWGGA (Hartree-Fock exchange and PWGGA correlation) band structure; (c) xcPWGGA (PWGGA exchange-correlation functional) band structure.

**TABLE 1: Mulliken Population Analyses for the Valence Orbitals Obtained with the  $\text{AE}^*$  Basis Set in the Three Approximations: HF, xHF-cPWGGA (Hartree-Fock exchange and PWGGA correlation) and xcPWGGA (PWGGA exchange-correlation functional)**

atoms		Si [Ne] $3s^2 3p^2$			Mg [Ne] $3s^2$	
number of electrons of valence		4			2	
atomic orbitals		s	p	d	s	p
$\text{AE}^*/\text{HF}$	$Z^a$		5.77		1.115	
	$Z_{\text{OA}}^b$	1.841	3.911	0.023	0.483	0.632
$\text{AE}^*/\text{xHF-cPWGGA}$	$Z$		5.673		1.163	
	$Z_{\text{OA}}$	1.798	3.847	0.028	0.492	0.671
$\text{AE}^*/\text{xcPWGGA}$	$Z$		5.324		1.338	
	$Z_{\text{OA}}$	1.773	3.478	0.073	0.572	0.766

<sup>a</sup>  $Z$ : number of electrons assigned to each atom. <sup>b</sup>  $Z_{\text{OA}}$ : number of electrons assigned to each atomic shell.

a single lattice constant  $a$  has to be optimized through the minimization of the crystal energy. The effect of taking correlation into account is to contract the crystal, i.e., to decrease the lattice parameter that becomes gratifyingly closer to the experimental value. For this parameter extracted from the first energy derivative, “hybrid” methods ii and iii yield even better corrections than “pure” DFT (method iv), although this may be by chance. In each approximation, it is noticed that the optimized values of the lattice parameters obtained with the  $\text{PP}^*$  basis set are systematically overestimated with respect to experiment. The results are better with the  $\text{AE}^*$  basis set. This can be assigned to the fact that core relaxation is neglected when effective core pseudopotentials are used.<sup>24,48,49</sup>

The elastic constants  $C_{ij}$  are related to the energy second derivatives according to  $1/V_0[\partial^2 E/\partial\eta_i\partial\eta_j]_0$ ;  $V_0$  is the volume of the primitive cell and the strain components  $\eta_i$  ( $i = 1, \dots, 6$ ) are related to changes in the six unit cell constants, due to the lattice strain (the method is described in refs 2, 50, and references therein). The vibrational frequencies of the two transverse optical modes at the center of the Brillouin zone, one Raman active ( $\nu_R$ ) and one IR active ( $\nu_{\text{IR}}$ ), were calculated within the frozen phonon approximation. The harmonic force constants were obtained from polynomial fit of  $E$  against the normal modes of vibration. The dynamic matrix was then diagonalized

to extract the frequencies. The results are presented in Table 2. As the phonons and elastic constants are directly connected,<sup>51</sup> the statements relating to the phonon frequencies given below can be extrapolated to elastic constants.

In  $\text{Mg}_2\text{Si}$ ,  $\nu_R$  is experimentally slightly smaller than  $\nu_{\text{IR}}$  (258.5 and 267  $\text{cm}^{-1}$ , respectively). At the HF level, the order of the values is reversed. This is a general trend for HF calculations of antiferroite and ferroite<sup>52</sup> vibrational frequencies. But, at least in the case of  $\text{Mg}_2\text{Si}$  and for the calculations using  $\text{AE}^*$  basis set (though not for those using the  $\text{PP}^*$  basis set), this anomaly generally disappears when correlation effects are taken into account.

In a previous paper limited to the Hartree–Fock level,<sup>2</sup> it was found that the  $C_{12}$  and  $C_{44}$  elastic constants related with torsions and shears are poorly calculated within the mono-electronic representation (the HF errors compared to experimental values are respectively  $\approx -41\%$ , and,  $\approx -6\%$  for  $\text{PP}^*$  and  $\approx +23\%$  and  $\approx +20\%$  for  $\text{AE}^*$ ); the HF calculated frequencies differ by almost 10% from experimental values, which is the order of magnitude of what is usually found in the HF approximation.<sup>53–55</sup>

As expected, the values of frequencies calculated via DFT<sup>20,47,53,55,57</sup> are better than HF ones (largest errors for  $\nu_R$  and  $\nu_{\text{IR}}$  are respectively  $\approx +7\%$  and  $\approx 5\%$ ). Similarly, except for  $C_{12}$  and  $C_{44}$  calculated with the Becke-LYP exchange-correlation functional, the calculated values of the elastic constants are satisfactory. In fact, intraatomic correlation plays an important role for the description of the force constants of the semiconductor,<sup>1</sup> so that the calculations with exchange-correlation functionals (method iv) are quite convenient to describe this kind of electronic ground-state property.

In contrast with “complete” DFT, “hybrid” methods ii and iii are not really efficient to correct the error of the HF approximation on second energy derivatives, especially when inner atomic displacements are required for full energy relaxation ( $C_{44}$  constant) or imposed to simulate vibration (vibrational frequencies). This problem is connected to the fact pointed out above that it is inadequate to associate a correlation functional developed for DFT with the “exact” HF exchange energy because the partition between exchange and correlation energies is not the same in the HF and KS methods.<sup>42</sup> In the Kohn–

**TABLE 2: Structural Properties, Elastic Constants, and Raman and Infrared Frequencies Calculated with Selected Basis Sets Using Various Exchange and Correlation Energy Density Functionals (labels explained at the bottom of the page)**

	lattice constant (Å)	bulk modulus B (GPa)	elastic cst C <sub>11</sub> (GPa)	elastic cst C <sub>12</sub> (GPa)	elastic cst C <sub>44</sub> (GPa)	Raman frequency $\nu_R$ (cm <sup>-1</sup> ) ( <i>T</i> = 300 K)	infrared frequency $\nu_{IR}$ (cm <sup>-1</sup> ) ( <i>T</i> = 300 K)
EXP <sup>a</sup>	6.338	59	126	26	48	258.5	267
Hartree–Fock Approximation <sup>b</sup>							
AE*	6.430	60	150	20	58	284	272
PP*	6.506	58	147	15	45	280	251
Hartree–Fock “Exact Exchange” + <i>A Posteriori</i> Correlation Energy							
AE*/CS <sup>c</sup>	6.277	71	182	14	66	294	298
PP*/CS	6.427	63	146	25	56	292	272
AE*/PWGGA <sup>d</sup>	6.244	71	179	22	68	306	317
PP*/PWGGA	6.404	64	144	22	56	302	286
AE*/LYP <sup>e</sup>	6.284	70	175	16	65	302	292
PP*/LYP	6.427	64	145	25	56	290	272
Hartree–Fock “Exact Exchange” + Correlation Energy Density Functionals							
AE*/xHF-cVWN <sup>g</sup>	6.319	65	155	20	59	299	301
PP*/xHF-cVWN	6.420	64	147	23	56	292	268
AE*/xHF-cPWGGA	6.262	73	193	14	68	315	326
PP*/xHF-cPWGGA	6.404	64	150	20	58	298	299
AE*/xHF-cLYP	6.277	63	151	19	68	313	299
PP*/xHF-cLYP	6.427	65	148	24	56	293	272
Exchange and Correlation Energy Density Functionals							
AE*/xLDA <sup>h</sup> -cVWN	6.286	54	130	20	50	270	282
PP*/xLDA-cVWN	6.482	60	124	22	45	279	263
AE*/xcPWGGA	6.398	59	136	18	52	269	265
PP*/xcPWGGA	6.481	64	125	31	47	277	259
AE*/xBECKE <sup>i</sup> -cLYP	6.439	50	116	18	50	252	264
PP*/xBECKE-cLYP	6.505	56	148	14	52	276	245

<sup>a</sup> Experimental data (extrapolated to *T* = 0 K) are provided in line 2 for comparison: refs 43, 40. <sup>b</sup> AE\* is an all-electron basis set; PP\* is a basis set associated with Durand–Barthelat pseudopotentials: refs 2, 12–15. <sup>c</sup> CS: Colle–Salvetti correlation density function: refs 26, 27. <sup>d</sup> PWGGA: Perdew Wang Generalized Gradient Approximation: refs 29–31. <sup>e</sup> LYP: Lee Yang Parr: ref 28. <sup>f</sup> x stands for exchange functionals, and c for correlation functionals. <sup>g</sup> VWN: Vosko–Wilk–Nusair: ref 32. <sup>h</sup> LDA: local density approximation: ref 33. <sup>i</sup> BECKE: Becke exchange function: ref 34.

Sham theory, the correlation is overestimated (compared with the traditional HF correlation energy definition) while exchange is underestimated.<sup>42</sup> Moreover, it has been recently argued by Gritsenko et al.<sup>58,59</sup> that the DFT (GGA) exchange functionals seem, inadvertently, to incorporate part of the correlation energy. The functionals for correlation happen to lack this part. Therefore the sum can be used, but not the exchange and correlation functionals individually. When HF exchange is combined with a DFT correlation functional, such a balance does not appear, hence the results are incorrect. However, it is symptomatic that an *a posteriori* correction of HF exchange calculated with a correlation functional designed just for that purpose (like the Colle–Salvetti functional) accentuates less the Hartree–Fock versus experiment deviation than does a correlation functional especially designed for DFT calculations (such as the PWGGA functional). Methods have been developed to retain at least partially the advantages of dealing with an exact HF exchange. Thus, the B3LYP functional,<sup>60</sup> in which HF exchange is mixed with an exchange–correlation functional, gives good results for molecules except perhaps for the dissociation energy (see for instance ref 56). Also Chan et al.<sup>61</sup> developed a molecular correlation potential adapted to HF exchange from *ab initio* coupled cluster densities via a modified Zhao, Morrison, and Parr scheme involving exact exchange.<sup>62</sup> Anyway, the development of theories able to deal more and more exactly with correlation remains a challenge in solid-state physics, and no doubt that progress remains desirable in this field.

#### 4. Conclusion

This body of SCF-HF/KS-LCAO calculations carried out with two basis sets and various exchange–correlation functionals

emphasizes the importance and difficulties in modeling and determining the correlation energy effects for a semiconductor like Mg<sub>2</sub>Si and more generally for any condensed matter system. This is especially so when one deals with properties directly related to the ground-state electronic potential energy surface of the crystal (phonons, elastic constants) and the excited states (band gap problem). It has been pointed out that the dynamic phenomena (properties related with variations around the equilibrium point of the electronic potential energy surface, for instance the phonon frequencies) are satisfactorily described by the Kohn–Sham theory.

It has been noticed that the addition of a correlation functional to the Hartree–Fock exchange (method ii or iii) does not correct efficiently — and may even worsen — the results obtained at the HF level. This has been assigned to the difference of definitions of the notion of correlation energy in DFT and in HF points of view and to the peculiar partition of exchange and correlation energies in DFT functionals.

It has been shown that *ab initio* calculations are a powerful tool for interpreting at a quantitative level the manifold of phenomena encountered in condensed matter physics.<sup>2</sup> But, the accuracy of the results significantly depends on the correlation effects. This justifies the efforts in progress to take into account correlation by adding a suitable correlation functional to the HF exchange. This would avoid the use of potentially exact but exceedingly demanding methods, like configuration interaction, which give excellent results for small systems limited to a few number of electrons but are difficult to use for large molecules and impossible to apply in the case of solids.

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