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# Ground state properties of Fluorine from DFT-hybrid

### functional

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### Abstract

The ground state properties of Calcium Fluorine (CaF<sub>2</sub>), such as structural, mechanical, optical, electronic and bonding properties, have been investigated by means of density functional theory (DFT). To overcome the important underestimation of the fluorine band gap evaluated from traditional DFT functional, we use here the hybrid exchange technique mixing DFT functionals and Hartree-Fock exchange through Heyd-Scuseria-Ernzerhof (HSE06) functional. The obtained results show good agreement with experimental data using HSE06 functional. Band structure and density of states (DOS) are given and the contributions of Calcium and Fluor atoms to DOS are analysed and compared to theoretical and experimental data. Based on the dielectric function calculations over the photon energy region up to 50eV, the hybrid functional was found to accurately reproduce the optical properties of CaF<sub>2</sub>. This provides a relatively inexpensive method to describe with high accuracy the behaviour of the fluorine system with respect to its electronic and optical properties. However, the structural and mechanical properties were underestimated and overestimated respectively using HSE06 functional, the best results were obtained using GGA-AM05 functional.

Keywords: Fluorine; DFT; hybrid exchange technique; ground state properties.

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#### I. Introduction

Calcium Fluoride (CaF<sub>2</sub>) is considered as one of the most important alkali fluorides with excellent UV transmission properties and sticking mechanical properties. This makes CaF<sub>2</sub> a compound of great interest in geoscience and an outstanding candidate for multispectral imaging application. The electronic structure and elastic properties of CaF<sub>2</sub> have been recently calculated from first-principles methods. At the beginning of the 1990s, a first *ab initio* study of the electronic and mechanical properties of CaF<sub>2</sub> was attempted by Catti et al. using Hartree-Fock theory [2]. Then, many ab initio based calculations of bulk electronic, optical and elastic properties have been performed [3-5] within full-potential calculation. More recently, Shi et al. [6] investigated the pressure-induced structural phase transitions, electronic structures and elastic properties of CaF2 using ab initio where the core electrons together with the nuclei were described from pseudopotentials in the framework of the PAW method. However, the obtained results underestimate the band gap (7.3 eV) at zero pressure compared with experiment data (11.8 eV). Nevertheless, many studies require precise accurate electronic calculation, especially in the field of defect engineering. Hence, to get a reliable basis for such calculations, we use here the screened hybrid-functional of Heyd, Scuseria, and Ernzerhof (HSE06) [7] that overcomes the inherent band gap underestimation of traditional functionals such as the local-density approximation (LDA) or generalized-gradient approximation (GGA). From experimental point of view, recently Sandhu et al. [8] realised reactive faceted nanosized titania with enhanced photocatalytic performance under fluorine free conditions.

In this paper, we are investigating the entire ground state properties of fluorine under zero pressure, i.e. at ambient conditions, using several DFT functionals. In the aim of getting a precise description of electronic properties and thus a careful analysis of bonding characters of the system, we used the HSE06 hybrid functional. The corresponding results are presented in the  $3^{rd}$  section of this paper as follows: in the  $1^{st}$  subsection, the optimized geometry of the system is calculated and structural properties are deduced. In the  $2^{nd}$  subsection, mechanical properties, such as elastic constants of fluorine are determined. The  $3^{rd}$  subsection collects the electronic quantities of the system. Finally, the  $4^{th}$  subsection analyses the bonding characters based on the obtained charge density. Section IV is the conclusion.

#### **II.** Computational method

First principles calculations on CaF<sub>2</sub> were performed here using the Vienna *Ab Initio* Simulation Package, VASP [9,10] based on density functional theory (DFT). The Kohn–Sham equations were solved variationally with a plane-wave (PW) basis set in the projector-augmented-wave (PAW) method [11]. The exchange and correlation function is treated using various DFT functionals: the local density approximation (LDA) [12] and the generalized gradient approximation (GGA) [13] (We employed both PBE [13] and AM05 [15]). Additionally, we used the Heyd–Scuseria–Ernzerhof (HSE06) [7] screened-Coulomb hybrid density functional for electronic and optical structure calculations. In fact, HSE has proven to reproduce band gaps with a high degree of accuracy [16]. Convergence of the total energies (within  $10^{-5}$ eV/atom) was reached with respect to cut-off energy of 600 eV. The Brillouin zone was sampled with a 16x16x16 K-points automatically generated mesh using Monkhorst Pack [17]. The geometry relaxation of atomic positions and the volume shape optimization were performed using a conjugate gradient algorithm with a stopping criterion of  $10^{-7}$  eV for the total energy.

### III. Results and discussions

#### a. Structural Properties :

Experimental data obtained by Speziale and Duffy [18] were used to set the initial structure of fluorine for the structural relaxation calculations. For each DFT functional, the structure was completely relaxed. We report in Table 1 the optimized lattice cell constant with comparison to the available experimental and other works data. We can see that LDA calculation underestimates  $a_0$  by 2.9% while GGA functional shows a slight overestimation of  $a_0$  by 0.7%. The hybrid functional HSE06 slightly underestimates the lattice parameter by 0.7% while the AM05 functional gives the best approximation of  $a_0$  within only 0.4% underestimation. Finally, the optimized structure of CaF<sub>2</sub> is displayed in Fig.1.

#### b. Mechanical properties

The elastic tensor is determined by performing six finite distortions of the lattice and by deriving the elastic constants from the strain-stress relationship. The method is discussed in detail in reference [18]. For small deformations the linear relationship between the stress tensor components and the strain tensor can be written  $\sigma_i$ following Hooke's law:

$$\sigma_i = C_{ij} \mathcal{E}_j \tag{2}$$

Due to the cubic symmetry  $CaF_2$  has three independent elastic moduli tensor coefficients:  $C_{11}$ ,  $C_{12}$  and  $C_{44}$ . Thus, several elastic properties can be calculated once the elastics constants are obtained.

The Voight and Reuss schemes representing respectively the upper and lower limit of the bulk (B) and shear modulus (G) are calculated in terms of elastic moduli tensor and compliance matrix (inverse of the elastic moduli tensor) coefficients  $C_{ij}$  and  $S_{ij}$ , respectively [20,21]:

$$K_{voight} = \frac{C_{11}}{3} + \frac{2C_{12}}{9} \tag{3}$$

$$K_{\text{Reuss}} = \frac{1}{3S_{11} + 6S_{12}}$$

5

$$G_{voight} = \frac{C_{11} - C_{12}}{5} + \frac{3C_{44}}{5}$$
(5)

$$G_{\text{Reuss}} = \frac{5}{4S_{11} - 4S_{12} + 3S_{44}} \tag{6}$$

Using Hill definition, the values of bulk and shear modulus retained are the average between both Voight and Reuss values [22]:

$$K_{Hill} = \frac{K_{Voight} + K_{Reuss}}{2}$$

$$G_{Hill} = \frac{G_{Voight} + G_{Reuss}}{2}$$
(7)
(8)

Once shear and bulk moduli are obtained, the Young modulus (E) and the Poisson ration ( $\mu$ ) can be deduced using the relationships:

$$E = \frac{9BG}{3B+G} \tag{9}$$

$$\mu = \frac{3B - 2G}{2(3B + G)} \tag{10}$$

Calculated parameters with different DFT functionals are reported in Table 3 and compared to experimental and theoretical data. The cited experimental data were obtained by the Brillouin Scattering (BS) [23] method and are then extrapolated to 0° K [2] since the temperature effects are not taken into consideration in this analysis. We note that obtained C<sub>44</sub> includes the inner relaxation effects. Observing the obtained values, we see that the GGA functional underestimates the elastic constants, especially C<sub>44</sub> (nearly by -21%); while a significant overestimation is noticed by the LDA functional. This can be explained comparing the calculated cell parameter (a<sub>0</sub>) by the two functional with respect to the experimental value. The larger calculated a<sub>0</sub> from GGA produces a less rigid crystal; whereas a smaller calculated a<sub>0</sub> describes a more rigid structure and thus higher elastic constants values are obtained in such a case. The same comment applies to other *ab initio* calculations using the same functionals based on full potential method [3]. The HSE06 hybrid functional produces even a more rigid structure than LDA with significant deviations from the experiment. The best mechanical properties were found using the AM05 functional as the calculated elastic constants compare very well with experiment.

#### c. Electronic properties

In order to determine the main electronic band gap, we have performed DOS calculations using different functionals and then compared the results with experimental data. We summarise the obtained band-gap data in Table 2. GGA calculations show a band-gap of 7.6 eV. This value is much lower than the experimentally observed 11.8 eV [24] due to the well-known shortcoming of the DFT using GGA [25]. LDA functional also gives an underestimated band gap value of 7.8 eV, which is widely expected. Finally HSE hybrid functional calculations give an indirect band gap value of 9.90 eV that is in good agreement with experiment. For those reasons we have used for the analysis of electronic properties exclusively HSE hybrid functional, which includes a portion of exact Hartree-Fock HF exchange and consistently provides excellent results [26].

Fig.2 shows the calculated partial density of states (DOS) of Fluor. The valence region, below Fermi's energy, can be split into two main parts. The first one consists of a very sharp peak lying between -25.0 eV and -20.0 eV due to s states. The second part lies between -7.0 eV and 0.0 eV and it is a mixed contribution of s and p states. The conduction region, above the Fermi's region is mainly due to p states.

Fig.3 shows the partial DOS of Calcium. The valence region consists of small distant peaks. The conduction region is mainly due to d states with a low contribution of s and p states. Two main peaks can be observed. A very high DOS peak is situated around 10.0 eV-15.0 eV derives from d states; while a lower DOS peak lying between 30.0 eV and 35 eV is due to p states.

Fig.4 shows the total DOS of The  $CaF_2$ . The valence region is dominated by the Fluor contribution. Instead, the conduction region is essentially due to calcium atoms with a very low Fluor contribution. We may see that there are no important overlaps between Fluor and Calcium atoms in the DOS and that the occupied bands are almost pure atomic like-states, which agree with the results of Shi et al. [4].

From the band structure calculations (Fig.5) within HSE functional, it is found that the gap of  $CaF_2$  is indirect with CB minimum at the point X and VB maximum at Gamma point.

#### d. Bonding properties

Using the Bader charge analysis, we calculated the partial charges of the atoms. We can see from Table 4, for all functionals, that the obtained values are close to the ionic charges : +2e for Ca<sup>2+</sup> and -e for F<sup>-</sup>, confirming the high ionic character of the Ca-F bond due to the important electronegativity difference ( $\chi_F$ =3.98 and  $\chi_{Ca}$ =1.0 according to Pauling scale) [27].

Then, we visualize the charge density projection onto the (0 1 1) plane using HSE06 functional. Fig.6 shows the electronic charge density from the (0 1 1) side that points out again the ionic character of the system. Fig.7 represents the charge density map on the same chosen plane. The charge density is significantly high around the atoms. In contrast, the electronic charge density is less important between the atoms, which is in agreement with the bond analysis done by Catti et al. [2] leading to a very low Ca-F bond character.

#### e. Optical Properties:

Optical properties are tightly related to electronic properties. A Reliable description of the optical properties is conditioned by the choice of the functional that calculates accurately the electronic properties. Therefore, HSE06 was selected for calculating the optical properties of CaF<sub>2</sub> based on the real  $\varepsilon_1(w)$  and imaginary  $\varepsilon_2(w)$ 

parts of the dielectric function  $\varepsilon(w)$ . The energy loss function  $L(\omega)$  is given by:

$$L(\omega) = \frac{\varepsilon_2(\omega)}{|\varepsilon(\omega)|^2} \qquad (11)$$

Fig.8 shows the dielectric function for radiation up to 50eV. The static dielectric constant  $\varepsilon_0$  determined from the real function part at low frequency  $\varepsilon_1(0)$  has a value of 1.82 which is only 11% smaller than the experiment value ( $\varepsilon_0=2.04$ ) [30]. A more important disparity was observed for the  $\varepsilon_0$  value (1.49) using LDA functional with the scissor operator shifts for band gap correction [31].

An overall shape resemblance of the dielectric function is observed with the experimental curve by Stephan el al. [32]. The calculated  $\varepsilon_2(w)$  exhibits a first group of three peaks laying at 11.04; 12.92 and 14.2eV with a central pronounced peak that corresponds to a  $\Gamma$  valence exciton while the peaks at higher energies are associated to inter-band transitions. The highest peak of the loss-energy function at 37.8eV (Fig.9) is associated with a plasma oscillation. At this photon energy,  $\varepsilon_1(w)$  increases from negative values while  $\varepsilon_2(w)$  is very low. The same result was pointed by experimental studies [32,33]. However, there is a small difference in the peak position that was found at 36.4eV by Stephan et al.[33] and at 35.8eV by Frandon et al. [33].

#### **IV.** Conclusion

We have studied the ground state properties of fluorine by means of ab initio calculations. The importance of using a hybrid functional to describe the electronic, bonding and optical properties has been demonstrated by the great agreement noticed with the experimental band gap value. The eigenvalues of electronic states are thus well described using this functional and give a highly accurate band structure calculation. Theoretical studies using self-consistent orthogonalized linear combination of atomic orbitals (OLCAO) method within the LDA approximation have proven that introducing the band gap correction negatively affected the optical transition calculations [31]. In contrast, the hybrid functional was found to be successful for both overcoming the gap underestimation and accurately reproducing the optical properties. Thus, the presented functional within the pseudopotential formalism provides a reliable tool for accurate electronic and optical calculations at much lower computational coast compared to the full-potential approach. In the other hand, HSE was less accurate for predicting the mechanical properties of CaF<sub>2</sub> than the standard DFT functionals.

### Tables

Table 1: Calculated lattice constant  $(a_0)$ , bulk modulus (B), pressure derivate (B') of CaF<sub>2</sub> compared to experimental and other works data.

		This work			Theoretical data			
	Experimental	LDA	GGA-	GGA-	HSE	LDA	GGA-	GGA-FPL
	data [28, 29]		PBE	AM05	06	[4]	PBE	APW
							[4]	[3]
a <sub>0</sub> (Å)	5.46	5.30	5.50	5.44	5.42	5.34	5.52	5.51

Table 2: Calculated elastic constants, Bulk modulus (B), isotropic shear modulus (G), Young's modulus (E), Poisson's ratio (v) and the comparison with other works data. BS' refers to BS extrapolated at 0 K.

	This work			Theoretical data			Experimental data		
	GGA-PBE	LDA	AM05	HSE06	GGA-LCAO[3]	LDA-PP[3]	HF[2]	BS[23]	BS'[2]
C <sub>11</sub> (GPa)	154.67	189.05	159.84	197.77	158.5	183	172.2	165.5	173
C <sub>12</sub> (GPa)	39.94	57.69	41,01	65.24	39.7	61	38.6	38.9	40.5
C <sub>44</sub> (GPa)	29.51	38.33	30.94	45.71	35.1	34	44	33.5	37.5
B (GPa)	78.18	101.48	80.19	93.56					
G (GPa)	38.64	47.63	40.32	53.16					
E (GPa)	99.52	123.56	103.6	134.09					
ν	0.29	0.3	0.28	0.26					

Table 3: Calculated band gap of fluorine using several functionals and compared with experimental data.

	Experimental [23]	GGA-PBE	GGA-AM05	LDA	HSE06
$\Delta_{g}(eV)$	11.8	7.10	7.26	7.3	9.90

Table 4: Partial charges of fluorine atoms.

	Partial charge (e)					
	GGA	LDA	AM05	HSE06		
Ca	1.7142	1.6853	1.7094	1.7569		
F	-0.8571	-0.8426	-0.8574	-0.8784		

## **Figures caption**

- Fig. 1: Optimized structure of Fluorine.
- Fig. 2: Partial DOS of Fluor with orbital contributions.
- Fig. 3: Partial DOS of Calcium with orbital contributions.
- Fig. 4: Total DOS of Fluorine with atomic contributions.
- Fig.5: Band structure of Fluorine using hybrid DFT functional.
- Fig.6: Charge density of Fluorine from the (0 1 1) side.
- Fig.7: Charge density map in the (0 1 1) plane.
- Fig.8: Calculated dielectric function of Fluorine.
- Fig.9: Calculated energy loss function  $L(\omega)$  of Fluorine



Fig. 1.



Fig. 2.



Fig. 3.



Fig. 4.



Fig. 5



Fig.6







Fig. 8



Fig. 9

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