



Trade Science Inc.

Materials Science

An Indian Journal

Full Paper

MSAIJ, 2(6), 2006 [192-196]

Hartree-Fock ab Initio Study Of The Electronic Structure Of Perovskite (LaNiO_3)

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Received: 16th November, 2006Accepted: 1st December, 2006Web Publication Date : 27th December, 2006Co-Authors

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ABSTRACT

In a previous paper [J.Mol.Struct.(Theochem) 671, 71, 2004] we reported a theoretical study effect in BaTiO_3 . In this report we studied of the electronic structure of the lanthanum niquelate (LaNiO_3) to investigate the piezoelectricity in this material. In the calculations we used the 20s14p/5s3p and 31s23p18d/17s11p7d gaussian basis sets for the O (³P) and La (²D) atoms, respectively, from literature in combination with the 30s19p13d/11s8p6d basis set for the Ni (⁵D) atom, obtained by generator coordinate Hartree-Fock (GCHF) method, to evaluate its quality in molecular studies through of total energy and orbital energies (ϵ_{HOMO} and ϵ_{LUMO}) of the ²NiO¹⁺ and ¹LaO¹⁺ fragments. Then, the 5s3p contracted n basis sets was enriched with one polarization function of d symmetry and the 11s8p6d and 17s11p7d basis sets were supplemented with one diffuse function by symmetry for the Ni and La atoms. Finally, theses basis sets were used to calculate the total energy, moment of dipole, and total atomic charges from LaNiO_3 in C_s space group. The analysis of those properties showed that is reasonable to believe that LaNiO_3 does not present piezoelectric properties.

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KEYWORDS

HF ab initio study;
Electronic structure
of perovskite;
 LaNiO_3 ;
Piezoelectric properties;
GCHF method.

INTRODUCTION

Barium titanate (BaTiO_3) was the first perovskite structure developed and is still widely used. The polymorphic forms of BaTiO_3 have been likened by Kay et al.^[4] to a displacement of the central Ti^{4+} ion within its oxygen octahedron towards one, two and then three of the six adjacent oxygen ions as the temperature is lowered. This is a simplification of the actual atomic displacements, but it is a useful first approximation for understanding the structure.

In the previous article^[2], we developed Hartree-Fock (HF) calculations to study the piezoelectric effect in BaTiO_3 and the obtained results offered evidences that the piezoelectricity in this perovskite can be caused by electrostatic interactions. The purpose of this article is to study of the electronic structure of the lanthanum niquelate (LaNiO_3) and offer some insight with aid of the theory into the investigation of this property in perovskites not yet experimentally investigated.

In this study of LaNiO_3 were used the 20s14p/5s3p and 31s23p18d/17s11p7d gaussian basis sets for O (^3P) and La (^3D) atoms, respectively, from literature^[3]. For Ni (^3D) atom, we applied the genetaror coordinate HF method^[4] to obtain the 30s19p13d gaussian basis set which was contracted to 11s8p6d. The quality of the contracted basis sets was evaluated in calculations of the total and orbital energies in the HF-Roothaan method^[5] for the $^2\text{NiO}^{1+}$ and $^1\text{LaO}^{1+}$ fragments. Then was done the addition of one d polarization function in the contracted basis sets for O atom and one diffuse function by symmetry for Ni and La atoms. Finally, the 5s3p1d, 12s9p7d, and 18s12p8d basis sets were used to calculate the dipole moments, total energy, and total atomic charges in LaNiO_3 in space group C_s that we used to verify possible piezoelectricity of this material.

Computational details

1. The construction of the basis sets to Ni (^3D) atom

In the GCHF method, the 1-electron functions are chosen as

$$\Phi_i = \int \psi_i(1, \alpha) f_i(\alpha) d\alpha \quad i=1,2,\dots,n \quad (1)$$

where ψ_i , f_i and n are the generator functions, the weight function and the size of the basis set, respectively. The application of eq. (1) to calculate expectation values using a slater determinant leads to the Griffin-Wheeler-HF (GWHF) equation

$$[\mathbf{F}(\alpha, \beta) - \epsilon_i s(\alpha, \beta)] f_i(\beta) d\beta = 0 \quad i=1,2,\dots,m \quad (2)$$

where the ϵ_i are the HF eigenvalues, and the Fock, $\mathbf{F}(\alpha, \beta)$, and overlap $S(\alpha, \beta)$, kernels are defined in Ref.^[4].

The GWHF equations are integrated numerically through discretization integral with a relabeling of the generator space^[6]

$$\Omega = \ln \alpha / A \quad A > 1 \quad (3)$$

where A is a scaling factor.

The Ω space is discretized in an equally space mesh formed by Ω values so that

$$\Omega = \Omega_{\min} + (j-i) \Delta \Omega \quad j=1,2,\dots,N \quad (4)$$

In Eq.(4), N corresponds to the number of discretization points defining the basis set size, Ω_{\min} is the initial point and $\Delta \Omega$ the increment.

In the solution of the discretized form of Eq. (2), the (30s19p13d) basis set was used as defined by the mesh of Eq. (3). The discretization parameters (which define the exponents) for the basis set built to Ni (^3D) are: $\Omega_{\min(s)} = -0.5730$, $\Delta \Omega_{(s)} = 0.1195$, and $N_{(s)} = 30$; $\Omega_{\min(p)} = -0.2400$, $\Delta \Omega_{(p)} = 0.1098$, and $N_{(p)} = 19$; $\Omega_{\min(d)} = -0.3560$, $\Delta \Omega_{(d)} = 0.1192$, and $N_{(d)} = 13$.

2. Contraction of the 30s19p13d/11s8p6d basis set and evaluation of the quality of the contracted basis sets in polyatomic calculations

The contraction 30s19p13d was implemented by employing the segmented contraction scheme proposed by Dunning et al.^[7]. The same was contracted to 11s8p6d through the contraction scheme 14, 3, 3, 3, 1, 1, 1, 1, 1, 1/12, 1, 1, 1, 1, 1, 1, 1/8, 1, 1, 1, 1, 1.

The 30s19p13d and 11s8p6d basis sets were obtained through a slightly modified version of the ATOMSCF program of Pavani et al.^[8].

In order to evaluate the quality of the 5s3p[3], 11s8p6d, and 17s11p7d [3] basis sets in molecular studies, we accomplished calculations of total energy, highest occupied molecular orbital (HOMO) energy, and one level below to highest occupied molecular

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TABLE 1: Total and HOMO and HOMO-1 energies (hartree)

Fragment	Basis	Total energy	ϵ_{Homo}	$\epsilon_{\text{Homo-1}}$
$^2\text{NiO}^{+1}$	[11s8p6d] ^a /	-1581.44719657	-0.30512	-0.36298
	[5s3p] ^b			
$^1\text{LaO}^{+1}$	(30s19p13d) ^c /	-1581.49041709	-0.33790	-0.37259
	(20s14p) ^d			
$^1\text{LaO}^{+1}$	[17s11p7d] ^e /	-8295.70200640	-0.15106	-0.20323
	[5s3p] ^b			
$^1\text{LaO}^{+1}$	(30s19p13d) ^f /	-8295.83581618	-0.0520	-0.17406
	(20s14p) ^d			

^{a, c} Contracted and uncontracted basis for Ni (⁵D) atom.

^{b, d} Contracted and uncontracted basis for O (³P) atom.

^{e, f} Contracted and uncontracted basis for La (²D) atom.

orbital (HOMO-1) energy for the $^2\text{NiO}^{+1}$ and $^1\text{LaO}^{+1}$ fragments at the HFR level^[5]. The results are compared with those obtained from the 20s14p^[3], 30s19p13d, and 31s23p18d^[3] basis sets.

In TABLE 1, the total and orbital energies for $^2\text{NiO}^{+1}$ and $^1\text{LaO}^{+1}$ fragments are shown. From this table, we can see that the total energies obtained with 11s8p6d/5s3p and 17s11p7d/5s3p basis sets are very close the corresponding values of 30s19p13d/20s14p and 31s23p18d/20s14p basis sets. The total energies differ by 43.2 and 133 milihartree for $^2\text{NiO}^{+1}$ and $^1\text{LaO}^{+1}$ fragments, respectively. The HOMO energies obtained from contracted basis sets are closer to those of the extended basis sets and differ by 32.7 and 99.1 milihartree for the $^2\text{NiO}^{+1}$ and $^1\text{LaO}^{+1}$ fragments, respectively. The HOMO-1 energies obtained from contracted basis sets are also closer to the values of extended basis sets and present deviations of 9.61 and 29.1 milihartree.

To better describe the properties of the LaNiO_3 in the implementation of the calculations it was necessary to include polarization function for the O (³P) atom. The polarization function values were extracted from the Gaussian primitive basis set. The adequate polarization function is chosen through successive calculations for the $[\text{LaNiO}_3]_2$ fragment by using different primitive functions, taking into account the minimum energy criterion. The polarization function obtained through the strategy described is $\alpha_d = 0.394317$.

The role of a basis set is crucial point in ab initio calculation of transition metal compounds, since the description of the configuration of the metal in the compound differs from the neutral state. The adequate

diffuse functions were obtained through the total energy optimization of the ground state anion Ni^{1-} (²S) and La^{1-} (³H) by HF method. The following diffuse functions for the 11s7p6d and 17s11p7d basis sets were determined for the Ni and La, respectively, using this strategy: $\alpha_s = 0.0158489$; $\alpha_p = 0.120226$; and $\alpha_d = 0.0602559$ and $\alpha_s = 0.0115080$; $\alpha_p = 0.0500034$; and $\alpha_d = 0.0288403$.

The [18s12p8d]/[12s9p7d]/[5s3p1d] basis set was used in the calculation of total energy, total energy, and atomic charges (obtained with Mulliken's population analysis^[9]) from $[\text{LaNiO}_3]_2$ fragment.

3. The fragment that represents the crystalline 3D periodic LaNiO_3 system

In previous work^[2], the fragment model (Figure 1) was used to simulate the necessary conditions of the existence piezoelectricity in BaTiO_3 as full solid. In this work, we use the same model to represent the crystalline 3D periodic LaNiO_3 system. The Ni atom is located in the center of the octahedron being wrapped up for six O atoms, disposed in the reticular plane (200), and two La atoms arranged in the reticular plane (100).

To study the crystalline 3D periodic LaNiO_3 system it is necessary to choose a fragment (or a molecular model), which represents adequately a physical property of the crystalline system as whole. The fragment $[\text{LaNiO}_3]_2$ was chosen because, after its optimization, the obtained structural parameters (interatomic distances) were close to experimental values with good precision. The study was developed according to the following strategy: (i) first, it was carried out the geometry optimization of the $[\text{LaNiO}_3]_2$ fragment in the C_s symmetry and 0.5 Å electronic state. (ii) finally, calculations single points were developed with the geometry optimized according to the descriptions shown in figure 1.

In figure 1 (I): (a) represents the $[\text{LaNiO}_3]_2$ fragment with the Ni atoms fixed in the space. (b) represents the $[\text{LaNiO}_3]_2$ fragment with the Ni atoms being moved +0.005 Å in the X axis, while the La and O atoms being maintained fixed. (c) represents the $[\text{LaNiO}_3]_2$ fragment in which the Ni atoms are moved from -0.005 Å in the X axis and La and O atoms being maintained fixed.

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RESULTS AND DISCUSSION

Figure 1 (II) represents the $[\text{LaNiO}_3]_2$ fragment with the bond lengths $\text{Ni}_1\text{-O}_3$, $\text{Ni}_1\text{-O}_4$, and $\text{Ni}_2\text{-O}_4$ shortened from 0.005 Å.

The geometry optimization was performed by using the Berny's algorithm^[10] and all molecular calculations in this work were carried out by HFR method as implemented in the Gaussian 94 program^[11].

For the objective of verify possible piezoelectric properties of perovskite (LaNiO_3), the Ni^{+3} central ion should be centersymmetric and the $[\text{LaNiO}_3]_2$ fragment polarise when submitted under mechanical stress. Firstly, we would like to bring attention for the comparison among the calculated bond lengths and the experimental values^[12]. For La-O and Ni-O bond lengths, our results are 2.4923 and 1.8493 Å, while the experimental values are 2.5491 and 1.9279 Å, respectively. The differences between the theoretical and experimental values are 0.057 and 0.079 Å. This show a good performance of molecular [18s12p8d]/[12s9p7d]/[5s3p1d] basis set to describe the geometry of the fragment studied.

In TABLE 2 are shown the dipole moments (in Debye) and the total energy (in hartree) from $[\text{LaNiO}_3]_2$ fragment. This is TABLE, one can see that the fragment with Ni^{+3} at (b) is unstable when compared at (a); this is evidence is confirmed by increase of the dipole moment. However, when the central ion is moved for the position c can to be verify that the fragment is 0.0255 hartree more stable than at (a). This indicates which the Ni^{+3} central ion is not centersymmetric. Still in TABLE 2 we can see that reducing the $\text{Ni}_1\text{-O}_3$, $\text{Ni}_2\text{-O}_4$, and $\text{Ni}_2\text{-O}_4$ bond lengths, the calculations in the atomic position d also not shown a deviation of atomic charges among the atoms of the $[\text{LaTiO}_3]$ fragment, besides the increasing of the dipole moment of the fragment. These results suggest that not there is a probable polarization of LaTiO_3 crystal when submitted under mechanical stress.

TABLE 3 shows the values of the partial charges of the atoms in the $[\text{LaNiO}_3]_2$ fragment with Ni^{+3} at a, b, and c positions and the Ni-O bond length reduced of 0.005 Å. According to table, when the Ni^{+3}

TABLE 2: Total energy (hartree) and dipole moment (Debye) from $[\text{LaNiO}_3]_2$ fragment

Ni atom position	Energy total	μ_x	μ_y	μ_z	μ
a	-19903,13905	-6,8622	0,5933	-2,4218	7,3011
b	-19904,88221	-3,0880	-0,7841	-0,2948	3,1996
c	-19904,16458	-5,8428	2,7466	-0,5012	6,4756
d	-19904,15616	-7,1179	-2,3934	-0,8216	7,5544

Figure 1: The octahedral $[\text{LaNiO}_3]_2$ fragment. (Ia): (a) represents the $[\text{LaNiO}_3]_2$ fragment with the Ni atoms fixed in the space; (b) represents the $[\text{LaNiO}_3]_2$ being moved +0.005 Å in the symmetry X axis, while La and O atoms are maintained fixed; (c) it presents the $[\text{LaNiO}_3]_2$ fragment in which the Ni atoms are moved from -0.005 Å symmetry X axis and La and O atoms are maintained fixed; (Ib): represents the $[\text{LaNiO}_3]_2$ fragment with the bond lengths $\text{Ti}_1\text{-O}_3$, $\text{Ti}_1\text{-O}_4$, and $\text{Ti}_2\text{-O}_4$ shortened from 0.005 Å.

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TABLE 3: Total atomic charges from $[\text{LaNiO}_3]_2$ fragment

Atom	a	B	c	d
Ni ₍₁₎	2,4834	2,8050	2,4072	2,7010
Ni ₍₂₎	0,0546	0,35765	0,30130	0,06935
La ₍₁₎	1,8768	1,8992	1,8618	1,9790
La ₍₂₎	1,6228	1,5551	1,5230	1,6096
O ₍₁₎	-1,1795	-1,2548	-1,2340	-0,99981
O ₍₂₎	-1,1988	-1,4094	-1,2402	-1,1378
O ₍₃₎	-0,79932	-0,75232	-0,95303	-0,95249
O ₍₄₎	-0,39491	-0,95485	-0,69781	-1,0172
O ₍₅₎	-1,1799	-0,98761	-1,0568	-1,0124
O ₍₆₎	-1,2853	-1,2579	-0,91162	-1,2391

central ion is deviate of the a position to b and c positions occur the rearrangement of the electronic density, without however to be clearly established a tendency in the migration of the atomic charges. On the other hand, in TABLE 3 one can see that when the Ni₁-O₃, Ni₁-O₄, and Ni₂-O₄ bond lengths are shortened, at atomic position (d), by a mechanical stress, also occur the rearrangement of the electronic density, however without again to verify the tendency clearly in the migration of the atomic charges in the material.

Thus, we suggest that metal-O distance in the $[\text{LaNiO}_3]_2$ fragment is formed by π -symmetry covalent bonds between 3d and 5d orbitals from Ni (⁵D) and La (²D) atoms, respectively, to p orbital from O (³P) atom in opposition to BaTiO₃ where it was verified those bonds were ionic. The ionic characteristic between Metal-O bonds is a fundamental condition to occurrence of piezoelectricity in our opinion, which is not observed in the perovskite (LaNiO_3).

CONCLUSIONS

In the HF study of the electronic structure of LaNiO_3 in the C_s symmetry and 5A' electronic state, the calculated results of the bond lengths showed a very good concordance with the experimental values from literature. Obtained values of the moment of dipole, the total energy, and the total atomic charges showed that is reasonable to believe that LaNiO_3 does not present behavior of piezoelectric material.

ACKNOWLEDGEMENTS

We gratefully acknowledge the financial support from the Brazilian agencies CNPq and CAPES. We employed computing facilities at the LQTC-UFPA, and CENAPAD-UNICAMP.

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