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A Periodic Density Functional Theory and Hartree−Fock Study of Alkali Halides with Gaussian Orbitals

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Periodic-density functional theory (DFT) and Hartree−Fock calculations have been performed on the alkali halides for the alkali metals Li, Na, K, and Rb and the halogens F, Cl, Br and I. Calculations were done with HF-optimized basis sets and DFT-optimized basis sets, at the HF, local DFT (LDFT), and nonlocal DFT (NLDFT) with the Becke exchange potential and the Perdew−Wang correlation potential. The HF and NLDFT results are similar for the lattice parameters, in general, by overestimating them. The LDFT method always underestimates the lattice parameters. As a consequence, the HF and NLDFT methods predict bulk moduli that are too small and the LDFT method predicts bulk moduli that are too large. The absolute error in the bulk moduli are larger at the LDFT level than at the other levels. Charge distribution maps have been calculated and analyzed. The maps clearly show that the main difference between the HF and DFT densities is in the treatment of exchange and that the nonlocal (gradient) corrections moderate this difference.

1. Introduction

Periodic Hartree−Fock molecular orbital calculations[1] in the past decade have shown that this method can be used to reliably characterize and analyze the electronic and structural properties of a wide class of crystalline compounds. However, it has also been well-established in the solid-state community that density functional theory (DFT) methods[2,3] provide a good treatment for many solid-state systems.[4,5] Recent software developments (CRYSTAL95[6]) allow us to compute the total energy of periodic systems at the DFT level in a self-consistent way. The periodic Kohn−Sham equations[7,8] can be solved by using exchange and correlation functionals including many of the most popular ones from molecular quantum chemistry. We have performed a systematic analysis by using both Hartree−Fock and density functional methods for the alkali halides, to (1) show the effect of electronic correlation on cohesive properties such as the lattice energy (LE), equilibrium lattice constants (a_o) and bulk moduli (B_o); (2) define the order of the relative error for each structural variable for the different levels of theory when the atomic numbers of the elements increase and the electronegativities change; and (3) determine if basis sets developed for molecular DFT calculations are transferable to solid state calculations as well as ascertaining whether those basis sets developed in previous periodic HF calculations can be used at the DFT level. The alkali halides are suitable for this kind of study as: (1) they are cubic and, for this reason, only one lattice variable must be varied in order to calculate the energy dependence on unit cell volume and (2) high-quality experimental data at low temperature are available.

2. Computationals Details

As described previously,[9] one of the most important characteristics of the program CRYSTAL is the way in which Coulomb interactions enter in the Fock operator. There is no *cutoff* in their evaluation and the only approximation is the transformation of the infinite series of bielectronic integrals into a monoelectronic series by using a multipolar analysis of the charge density. This infinite, monoelectronic series is then computed by Ewald techniques. This scheme, originally developed for periodic Hartree−Fock,[9,10] is now available for periodic DFT. The exchange−correlation functionals generate exchange-correlation potentials which enter in the Kohn−Sham equations with a complex analytic form. The analytic evaluation of the matrix elements of the associated operator is a common approach implemented in programs for molecular calculations but is too expensive for periodic systems.[8] For this reason, the exchange-correlation potential is constructed as a linear combination of contracted Gaussian-type orbitals, which results in the need for a "second" basis set, as well as the usual atomic basis set. A suitable choice for this fitting basis set is the so-called *even-tempered* basis set, a universal collection of Gaussian functions which are not atom-dependent, as originally proposed by Baerends and te Velde.[8,11] The alkali halides are cubic crystals, and require only s functions. Three basis sets (a set of four, eight and twelve functions for each independent atom) of this kind are available in CRYSTAL95 without the need for user specification of the even-tempered exponents. For our calculations, we adopted the largest basis set of twelve functions to ensure a small error in the fitting of the exchange-correlation potential for all compounds.

A relatively broad choice of exchange and correlation functionals is available in CRYSTAL95. Our calculations were done with two of the most popular combinations used in molecular DFT calculations. The first, the local DFT (LDFT) level, used Slater exchange and the Vosko Wilk and Nusair[12] fit of the correlation energy of the noninteracting electron gas. The second, the nonlocal or gradient corrected (NLDFT) level, used the Becke exchange functional[13] and the Perdew−Wang correlation functional.[14]

Two types of atomic basis sets have been used in this work. The first is a basis set developed and tuned with CRYSTAL92 in a previous analysis of alkali (Li, Na, and K) fluorides and chlorides at the Hartree−Fock level and the second is an

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ensemble of basis sets derived from molecular DFT calculations, the polarized double-ζ basis set DZVP.[15] Starting from the latter set, a full optimization of the exponents and contraction coefficients was then performed, for each cation, at the level of the isolated ion. This optimization was necessary because the outermost exponents are too diffuse and not suitable for periodic calculations where they are a source of severe numerical instability. The "ionic" optimizations ensure a better compromise between the accuracy of the description of ionic properties and the "well-mannered" size of the exponent of the outermost shells. We used the original DZVP basis sets for all of the anions because the exponents of the outermost primitive GTO are already very diffuse and the "ionic" optimization would increase that characteristic leading to numerical instabilities[9] for the periodic calculations. We did refine the outermost exponents using the bulk structure. Any remaining error in the DZVP basis sets would be reduced or eliminated by a subsequent refinement of the most diffuse exponents of the anions and cations in the actual crystalline environment. The exponents and contraction coefficients of the new basis sets are given as Supporting Information.

All of the calculations, both basis set optimizations in the crystals and equilibrium structure determinations, were performed by using tight tolerance parameters for the Coulomb and exchange series evaluations: 10^{-6} for the overlap and penetration threshold for Coulomb integrals and for the overlap threshold for exchange integrals, and 10^{-7} and 10^{-14} for the pseudo-overlap criterion requiring two different truncation thresholds for the two sums over the translation vectors which appear in the exchange contribution to the total energy (exchange series).[6] Self-consistency, in terms of the total energy of the unit cell, was defined as a change of less than 10^{-7} hartrees (2.721×10^{-6} eV) between the last two SCF cycles. The shrinking factor for the Monkhorst[16] net was set equal to 8 giving 29 **k** points in the reciprocal space. We also used a shrinking factor equal to 8 for the Gilat[17,18] net and 8 plane waves were used for the expansion of the eigenvalues e_k.

3. Results and Discussion

Lattice Constants. The equilibrium lattice constant a_0 and the bulk modulus B_o for all halides of Li, Na and K, are given in Table 1 with a basis set developed previously for periodic HF calculations[19] for the cations and anions (F^-, Cl^-). Such a basis is not available for the bromides and iodides, so the optimized DZVP basis set was used for these ions. The calculation of a_o and B_o requires that the dependence of E on the unit cell volume V is known. For this reason, E must be sampled for different values of a_0 and the couples of points (E,V) interpolated by a suitable fitting function. We used the primitive $E(V)$ function obtained by integration of the Birch–Murnaghan[20] equation-of-state for $P(V)$ where P is the pressure. In this expression for $E(V)$, the equilibrium lattice constant (the equilibrium volume is a function of a_o only) and bulk modulus enter as adjustable parameters in the fitting. The Hartree–Fock calculations show the following: (1) A progressive increase of the relative error in the evaluation of a_o from Li to K, keeping the anion constant. A similar trend is found when the anion is changed from F^- to I^- keeping the cation constant. (2) For a particular cation, the error increases dramatically from F^- to Cl^-, especially for lithium and sodium (0% for LiF and 3.1% for LiCl, 0.2% for NaF and 3.2% for NaCl). The increment in the error then becomes more regular going from the chloride to the iodide. (3) The relative error in a_o increases slowly from LiF to NaF, but jumps to 3.4% for KF.

TABLE 1: Equilibrium Lattice Parameters (a_o, in angstroms) and Bulk Moduli (B_o, in GPa) for Alkali Halides at the Hartree–Fock (HF), LDFT, and NLDFT Levels. Values in Parentheses are Percentage Errors[a]

		structural parameters			
		F	Cl	Br	I
Li	a_o exp	4.01	5.11	5.46	5.95
	HF	4.02 (+0.0)	5.27(+3.1)	5.67(+3.2)	6.22(+4.5)
	NLDFT	4.11(+2.2)	5.21(+2.0)	5.56(+1.8)	6.07(+2.0)
	LDFT	3.93(−2.2)	4.99(−2.3)	5.32(−2.6)	5.78(−2.9)
	$B_o$exp	69.9[b]	35.4[c]	26.3[d]	18.8[h]
	HF	76.7(+9.7)	31.1(−12.1)	24.8(−5.7)	20.1(+6.9)
	NLDFT	61.6(−11.9)	33.0(−6.8)	26.5(−0.8))	21.5(+14.4)
	LDFT	86.8(+24.2)	46.1(+30.2)	39.1(+48.7)	31.8(+69.1)
Na	a_o exp	4.61	5.60	5.93	6.41
	HF	4.62(+0.2)	5.78(+3.2)	6.16(+3.9)	6.73(+5.0)
	NLDFT	4.75(+3.0)	5.75(+2.6)	6.10(+2.9)	6.59(+2.8)
	LDFT	4.52(−2.0)	5.48(−2.1)	5.80(−2.2)	6.28(−2.0)
	B_o exp	51.4[c]	26.6[c]	22.6[c]	17.9[e]
	HF	50.9(−0.5)	23.7(−10.9)	18.0(−20.3)	14.6(−18.4)
	NLDFT	39.3(−23.5)	22.9(−13.9)	17.6(−22.1)	12.6(−29.6)
	LDFT	61.3(+19.3)	35.2(+32.2)	29.3(+29.6)	22.8(+27.4)
K	a_o exp	5.31	6.25	6.54	6.99
	HF	5.49(+3.4)	6.57(+5.1)	6.94(+6.1))	7.48(+7.0)
	NLDFT	5.57(+4.9)	6.55(+4.8)	6.88(+5.2)	7.37(+5.4)
	LDFT	5.26(−0.9)	6.18(−1.1)	6.49(−0.8)	6.93(−0.9)
	B_o exp	34.2[c]	19.7[f]	14.8[g]	12.7[f]
	HF	29.9(−12.6)	15.7(−20.3)	12.6(−17.1)	10.3(−18.9)
	NLDFT	23.6(−31.0)	14.2(−28.9)	11.4(−25.0)	8.6(−32.3)
	LDFT	40.4(+18.1)	25.2(+27.9)	19.9(+30.9)	16.1(+26.8)

[a] Basis sets for F^- and Cl^- anions and Li^+, Na^+, and K^+ cations developed previously[19] at the Hartree-Fock level. A modified DZVP basis set (see text text and Supporting Information) was adopted for Br^- and I^-. Lattices parameter at 4.2 K taken from ref 31. [b] Bulk moduli at 4.2 K taken from ref 32. [c] Bulk moduli at 4.2 K taken from ref 33. [d] Bulk moduli at 4.2 K taken from ref 34. [e] Bulk moduli at 4.2 K taken from ref 35. [f] Bulk moduli at 4.2 K taken from ref 36. [g] Bulk moduli at 4.2 K taken from ref 38. [h] Bulk moduli at 4.2 K taken from ref 39 (average value at room temperature).

These results can be explained by simple arguments derived from correlation effects. As the number of electrons in the asymmetric unit of the unit cell increases, the correlation effects become more important. It is well-known that the lack of pair correlations in the Hartree–Fock approach causes an overestimate of the lattice constants (equivalent to chemical bond lengths) in the periodic system. This provides a qualitative explanation as to why the error in a_o is always positive and increases when the atomic number of the cations or anions (or both) increase. The authors of the previous systematic study of alkali halides[19] (for fluorides and chlorides of Li, Na, and K) interpreted the dramatic increase of the error from fluoride to chloride in terms of a combination of different effects (one intratomic, another interatomic) of electron correlation as follows. First, the periodic array creates an electrostatic field around the anions, which reduces their size. This effect is stronger for F^- than for Cl^- because the latter is more diffuse as a consequence of the less effective nuclear attraction in the larger anion. The ionic radii for I^-, Br^-, Cl^-, and F^- are 2.20, 1.96, 1.81, and 1.33 Å, respectively.[21] Thus, the largest change in the shrinking effect is found going from F^- and Cl^- and is less pronounced as one goes down the periodic table. Second, the dispersion forces (which are intimately connected with electronic correlation) are proportional to the polarizability of the ions which increases from F^- to I^-. The cations would be affected by these two phenomena although one would expect smaller changes as there are no formal valence electrons on the cations.

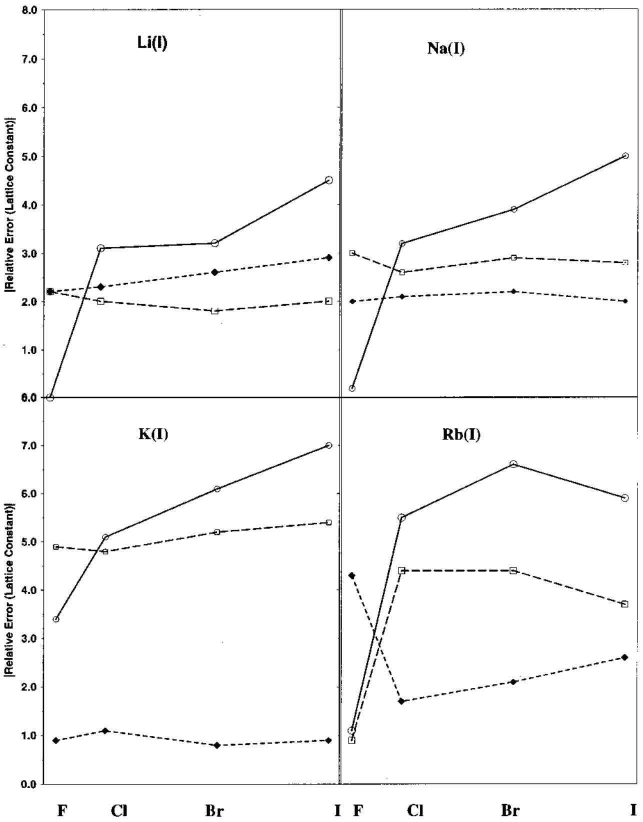

Figure 1. Absolute values of the relative errors, for each cation, in the lattice constant evaluation, as a function of the anions. The three sets of data are (a) HF (circles), (b) NLDFT (squares), and (c) LDFT (black diamonds). The LDFT values are actually negative.

TABLE 2: Ionic Character for the Alkali Halides

	F	Cl	Br	I
Li	89.4	69.2	62.1	50.5
Na	90.1	70.9	63.9	52.5
K	91.9	74.5	67.8	56.8

The DFT calculations of the equilibrium lattice constants exhibit different behavior. At the NLDFT level, the relative errors ($\Delta a\%$) are mainly controlled by the cations. For the Li compounds, $\Delta a\%$ is around 2.0% for all halides from F to I. The sodium and potassium halides show similar trends with the relative errors fluctuating around 3% and 5%, respectively. In all compounds, a_o is overestimated. The values for a_o at the local level are always smaller than the experimental values, but they do not show any particular regular trends. The percentage error increases in lithium compounds, from fluoride (−2.2%) to iodide (−2.9%), and fluctuates around an average value for the sodium (−2.0%) and potassium (−0.9%) halides. The average error is reduced in going from Li to K.

Figure 1 shows, for each cation, the absolute value of $\Delta a_o\%$ as a function of the anions. The plots were generated using the relative errors of Table 1 for Li, Na, and K (original CRYSTAL basis sets), whereas the rubidium data are from Table 3 (DZVP basis set). The four plots summarize the observations made during the analysis of Tables 1 and 3. The HF results are generally the best for the most ionic crystals, the fluorides. For the remaining halides, the LDFT method is the best and the errors are approximately constant for the LDFT and NLDFT methods except for RbF. In general, the NLDFT errors fall between the LDFT and HF relative errors. Figure 2 shows the same behavior of $\Delta a_o\%$, now as a function of the cations. The "shape" and relative positions of the three curves are almost the same for the chlorides, bromides, and iodides. The NLDFT and LDFT plots do not exhibit big changes from fluorides to iodides, if rubidium fluoride is excluded. The plot of the errors obtained at the NLDFT level is almost the same as the HF curve shifted to lower values (in particular for the sodium and potassium halides).

TABLE 3: Equilibrium Lattice Parameters (a_o, in angstroms) and Bulk Moduli (B_o, in GPa) for Alkali Halides at the HF, NLDFT, and LDFT Levels. Values in Parentheses are Percentage Errors (see Table 1)[a]

		structural parameters			
		F	Cl	Br	I
Li	a_o exp	4.01	5.11	5.46	5.95
	HF	4.02(+0.0)	5.27(+3.1)	5.63(+3.1)	6.31(+6.1)
	NLDFT	4.12(+2.7)	5.22(+2.2)	5.50(+0.7)	6.29(+5.7)
	LDFT	3.86(−3.7)	5.01(−2.0)	5.27(−3.5)	5.96(+0.1)
	$B_o$exp	69.9[c]	35.4[b]	26.3[d]	18.8[i]
	HF	76.7(+9.7)	32.0(−9.6)	27.5(+4.6)	18.1(−3.7)
	NLDFT	63.9(−8.6)	32.4(−8.5)	31.1(+18.2)	18.9(+0.5)
	LDFT	71.4(+2.2)	45.5(+28.5)	40.3(+53.2)	25.9(+37.8)
Na	a_o exp	4.61	5.60	5.93	6.41
	HF	4.62(+0.2)	5.78(+3.2)	6.15(+3.7)	6.70(+4.5)
	NLDFT	4.73(+2.6)	5.75(+2.7)	6.08(+2.5)	6.59(+2.8)
	LDFT	4.50(−2.4)	5.48(−2.1)	5.74(−3.2)	6.29(−1.9)
	B_o exp	51.4[b]	26.6[b]	22.6[b]	17.9[e]
	HF	50.9(−0.5)	23.5(−11.6)	18.8(−16.8)	17.7(−1.1)
	NLDFT	43.6(−15.2)	22.9(−13.9)	19.2(−15.0)	14.0(−21.8)
	LDFT	65.6(+27.4)	35.1(+32.0)	35.8(+58.4)	22.2(+24.0)
K	a_o exp	5.31	6.25	6.54	6.99
	HF	5.49(+3.4)	6.57(+5.1)	6.93(+6.0)	7.46(+6.7)
	NLDFT	5.56(+4.7)	6.54(+4.6)	6.86(+4.9)	7.14(+2.1)
	LDFT	5.24(−1.3)	6.18(−1.1)	6.47(−1.1)	6.76(−3.3)
	B_o exp	34.2[b]	19.7[f]	14.8[h]	12.7[f]
	HF	29.9(−12.6)	16.1(−18.3)	12.8(−15.8)	11.0(−13.4)
	NLDFT	25.1(−26.6)	15.0(−23.9)	11.3(−25.7)	9.9(−22.0))
	LDFT	42.0(+22.8)	26.7(+33.5)	21.2(+3.95)	20.4(+60.6)
Rb	a_o exp	5.59	6.53	6.82	7.26
	HF	5.65(+1.1)	6.89(+5.5)	7.27(+6.6)	7.69(+5.9)
	NLDFT	5.64(+0.9)	6.82(+4.4)	7.12(+4.4)	7.53(+3.7)
	LDFT	5.35(−4.3)	6.42(−1.7)	6.82(−2.1)	7.07(−2.6)
	B_o exp	30.1[g]	18.7[b]	16.0[b]	13.1[b]
	HF	34.7(+15.3)	14.4(−23.0)	8.8(−45.0)	10.9(−16.8)
	NLDFT	31.9(+4.0)	13.5(−27.8)	10.5(−34.4)	6.9(−47.3)
	LDFT	50.5(+67.8)	25.1(+34.2)	20.9(30.6)	19.1(+45.8)

[a] All calculations are carried out with DZVP[15] basis sets adapted (see text) for periodic calculations and given as Supporting Information. Lattices parameter at 4.4 K taken from ref 31. [b] Bulk moduli at 4.2 K taken from ref 33. [c] Bulk moduli at 4.2 taken from ref 32. [d] Bulk moduli at 4.2 K taken from ref 34. [e] Bulk moduli at 4.2 K taken from ref 35. [f] Bulk moduli at 4.2 K taken from ref 36. [g] Bulk moduli at 4.2 K taken from ref 37. [h] Bulk moduli at 4.2 K taken from ref 38. [i] Bulk moduli at 4.2 K taken from ref 39 (average value at room temperature).

Sodium chloride has been one of the most investigated structures by first-principles solid-state methods over the past two decades. Much of this work was done at the LDA (LDFT) level with plane−waves basis sets[22−27] instead of the Gaussian type basis sets, used in the present work. Table 4 reports results from these studies, and also those where the correlation effects were computed *a posteriori* by using the HF electron density with different correlation functionals. The full-potential augmented-plane−wave (FLAPW) method, with the Hedin−Lundquist correlation functional,[22] predicts a lattice constant that is larger than HF and our NLDFT result and as a consequence overestimates B_0. The other methods show a value of the lattice constant close (the difference is between +0.06 and −0.01 Å) to our LDFT value. The bulk modulus results with the plane−wave basis sets are in better agreement with experiment as compared to our LDFT value. A systematic study of the alkali halides[28] based on an approximate LDA formalism, exhibits

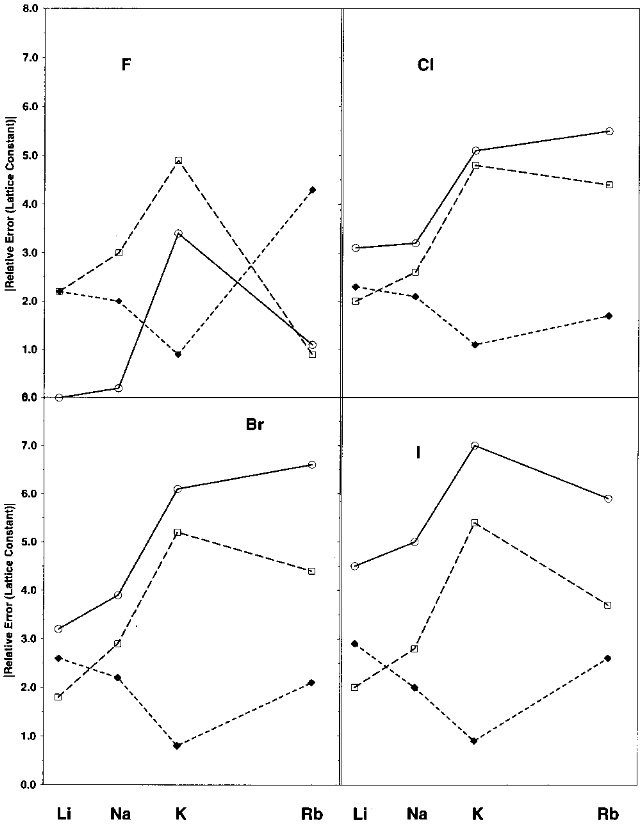

Figure 2. Absolute values of the relative errors, for each anion, in the lattice constant evaluation, as a function of the cations. The three sets of data are (a) HF (circles), (b) NLDFT (squares), and (c) LDFT (black diamonds). The LDFT values are actually negative.

TABLE 4: DFT Lattice Energies (LE, in kJ/mol), Lattice Constants (in angstroms) and Bulk Moduli (in GPa) of NaCl from the Literature[a]

method	functional	LE	a_o	B_o
PS-PW[b]	Wigner		5.52	31.2
FLAPW[c]	Hedin−Lundquist	783.5	6.64	30.4
LAPW[d]	Wigner		5.54	28.7
LAPW[e]	Hedin−Lundquist		5.47	31.4
NUM[f]	Ceperley-Alder	849.6	5.48	31.5
ASA + E[g]	Hedin-Lundquist		5.49	33.0
LCAO-HF[h]		744.2	5.80	22.8
LCAO-HF + P91[i]	Perdew(91) *a posteriori*	787.3	5.54	30.1
	Present Work			
LCAO-HF		817.1	5.78	23.7
LCAO-LDFT	Vosko−Nusair−Wilk	806.1	5.75	22.9
LCAO-NLDFT	Perdew−Wang	885.4	5.48	35.2
exptl		786	5.60	26.6

[a] PW = plane wave. FLAPW = full-potential linearized augmented plane wave. ASA + E = atomic sphere approximation plus total energy, within the linear muffin-tin orbital (LMTO) formalism. NUM = fully numerical method. P91 = Perdew correlation functional. [b] Ref 26. [c] Ref 22. [d] Ref 23. [e] Ref 23. [f] Ref 11. [g] Ref 27. [h] Ref 5.

good agreement with experiment, for both the lattice constants and bulk moduli for the halides of Li, Na, K, Rb, and Cs. In this approach, the charge density and the total energy are obtained without evaluating the Bloch states.

Bulk Moduli. The bulk modulus B_o can be expressed in terms of the inverse of the equilibrium volume and of the curvature of $E(V)$. Despite the dependence on the second derivative of E with respect to V, B_o should increase when the equilibrium volume of the unit cell decreases. As a consequence the overestimation (underestimation) of a_o (of V) induces a negative (positive) error in the evaluation of B_o. Figure 3 shows the distribution of the relative error ΔB_o% as a function of Δa_o%. Both HF and NLDFT methods exhibit a roughly linear trend with the error in B_o becoming more negative as Δa_o% increases. The LDFT results show a general increase in the error in ΔB_o% scattered around the interpolation curve as Δa_o% increases. Most of the error in B_0 is concentrated in the region of Δa_o% between −1% and −3%. The values of B_o for the alkali compounds, at the three levels of theory, are reported in Table 1. The HF (except for LiF and LiI) and NLDFT (except for LiI) methods underestimate the value of B_o, and HF seems to be more accurate for sodium and potassium halides, whereas NLDFT is more accurate for the lithium halides. By using local functionals for both correlation and exchange, the bulk modulus is always overestimated by 20−30%.

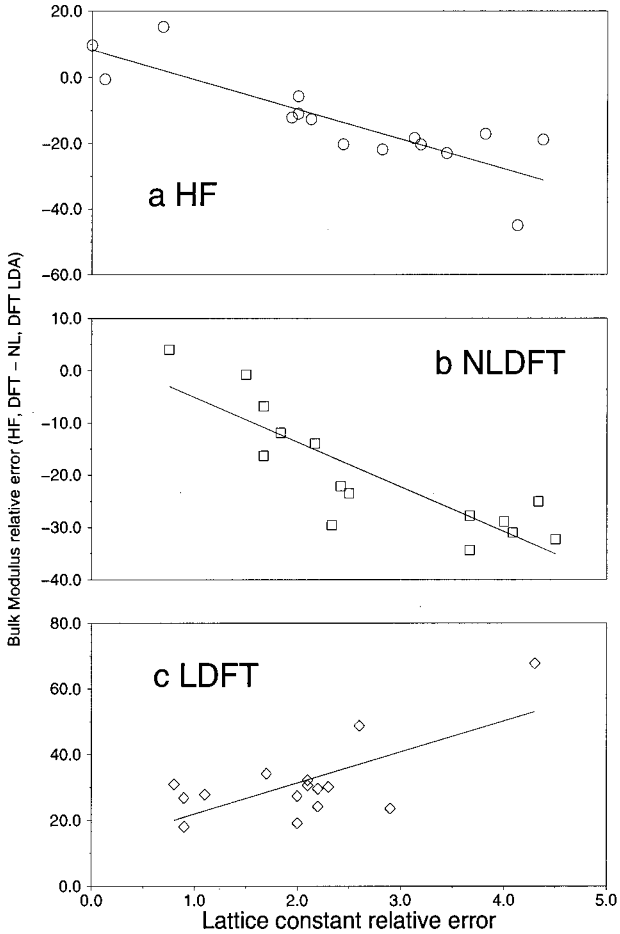

Figure 3. Relative errors in the bulk moduli evaluation, as a function of the lattice constant relative error. The three sets of data are (a) HF (circles), (b) NLDFT (squares), and (c) LDFT (diamonds).

There is very little correlation between the relative error of B_o with respect to the ionic character (Table 2) of the solids. The ionic character is obtained as a function of the electronegativity difference (EN) of the ions by using Pauling's electronegativities[29] and a polynomial fit (ninth degree) of ionic character vs the Pauling EN values.[30] The rubidium compounds have essentially the same values as the related potassium compounds. The sequence of data indicates that the M−X bond becomes more covalent for each cation as the size (atomic number) of the anion increases. For a particular anion, as the atomic number of the cation increases, the bond is more ionic. The latter effect is less important than the former and can be neglected.

The lattice constants and the bulk moduli calculated at the different levels of theory with the DFT (DZVP) basis sets on both cations and anions, are reported in Table 3. The results for the halides of Li, Na, and K follow, in general, the same trends as obtained by using the periodic HF basis sets. For LiI the different basis sets give different relative errors for a_o. The HF and NLDFT calculations of the lattice constant with the DZVP basis sets are larger than the HF-derived basis sets, but the LDFT value is now in better agreement with experiment. As a consequence, the bulk modulus is underestimated by a significant amount at the first two levels of theory and only a small error is found at the LDFT level (+0.8%) with this basis set. The analysis of Δa_o% trends show that for RbF, the errors differ from those found for the other rubidium halides. For the NLDFT results, we expected an overestimation of around 4%, yet the error is less than 1% and at the HF level the error is considerably smaller for RbF than the 3.5% and 5.5% errors found for KF and RbCl at the same level of theory. A careful comparison of Tables 1 and 3 shows other differences between the two results for the two types of basis sets. For LiCl and LiBr, the HF error is 3.1% for both basis sets, but the LDFT and NLDFT values of Δa_o% for LiBr differ from the errors found by using the periodic HF basis sets. In particular, the NLDFT level gives a smaller error, +0.7% with the DZVP basis set as compared to +2.0% with the HF basis set. The LDFT error is more negative with the DFT-derived basis sets as compared to the HF-derived basis sets. Although the NLDFT error in a_o for LiF exhibits little dependence on basis sets, the DZVP basis set gives a larger negative percentage error at the LDFT level as compared to the HF-derived basis set.

For the sodium compounds, the relative errors for the lattice constant are slightly improved by using the DZVP basis set, except for NaBr at the LDFT level. For the potassium compounds, KI displays, at the LDFT and NLDFT levels, the same behavior found for RbF. The error at the NLDFT/DZVP level is smaller than at the NLDFT/HF-basis level and the opposite is found at the LDFT level.

As found in Table 1, the relative deviations in the bulk modulus are, in general, a function of Δa_o%, because B_o depends on the volume. However, there are changes in ΔB_o% which cannot be easily rationalized in this way. For example, the positive error in a_o at the HF and NLDFT levels for RbF does not lead to an underestimation of B_o, but rather to an overestimation.

Mulliken Charges. Table 5 reports the net Mulliken charge on the cation [q(M)] (the anion charge [q(X)] is just the negative of the cation charge) and the bond populations along the shortest distance for cation−anion [q(M−X)]. The Hartree−Fock calculations, for all crystals, predict more ionic character than do the DFT calculations. The net charge on the ions at the HF level is always closer to the ideal charges of +1 and −1 than the DFT charges. The difference between the HF and DFT q(M) and q(X) values tends to decrease as the atomic number of the anion and/or the cation increases, which also corresponds to an increase in the lattice constant. For LiF the NLDFT charge is only one-half the HF value and the difference is even bigger for LDFT. This deviation drops to ≈0.1 e for the other three lithium halides. An analogous trend is found for the sodium compounds; the difference between the HF and NLDFT net charges is ≈0.23 e for NaF (0.29 for the HF/LDFT comparison) but on the order of 0.1 e for NaCl, NaBr, and NaI. As in the discussion of Δa%, we find again a remarkable difference in the description of fluorides of a particular cation with respect to the others halides. The net charge of Li^+ increases from the fluoride to the chloride, but for Na^+, $q(M)$ decreases, for K^+ there are no relevant changes, and for Rb^+, as for Na^+, a reduction of the net charge is predicted. We note that the largest difference between the DFT and HF methods for the charges are for lattice constants less than 5.0 Å.

TABLE 5: Mulliken Analysis (Net Charges and Bond Populations) for the Alkali Halides, at the Different Levels of Theory (for a Particular Crystal the HF, NLDFT, and LDFT Results Are the First, Second and Third Row, Respectively). All Data are in Electrons

		Li		K	
anion	method	q(M)	q(M−X)	q(M)	q(M−X)
F	HF	+0.862	−0.003	+1.007	−0.018
	NLDFT	+0.453	+0.009	+0.982	−0.006
	LDFT	+0.312	−0.003	+0.979	−0.007
Cl	HF	+0.944	+0.005	+1.006	−0.013
	NLDFT	+0.873	+0.015	+0.983	−0.006
	LDFT	+0.840	+0.016	+0.970	−0.005
Br	HF	+0.932	−0.014	+1.007	−0.013
	NLDFT	+0.824	+0.003	+0.988	−0.006
	LDFT	+0.754	+0.002	+0.979	−0.005
I	HF	+0.879	+0.016	+1.007	−0.009
	NLDFT	+0.816	+0.024	+0.991	−0.002
	LDFT	+0.786	+0.026	+0.980	−0.001

		Na		Rb	
anion	method	q(M)	q(M−X)	q(M)	q(M−X)
F	HF	+1.011	−0.019	+1.020	−0.044
	NLDFT	+0.784	+0.013	+0.937	−0.018
	LDFT	+0.717	+0.016	+0.925	−0.018
Cl	HF	+0.973	−0.004	+0.960	−0.006
	NLDFT	+0.883	+0.006	+0.905	+0.005
	LDFT	+0.814	+0.014	+0.878	+0.008
Br	HF	+0.951	−0.001	+0.978	−0.012
	NLDFT	+0.859	+0.008	+0.921	+0.001
	LDFT	+0.785	+0.016	+0.908	+0.003
I	HF	+0.932	+0.005	+0.961	−0.005
	NLDFT	+0.874	+0.009	+0.922	+0.008
	LDFT	+0.812	+0.017	+0.897	+0.011

The increase of the charge can be interpreted as the increase of the ionic character of the compound because the electrons are more depleted from the cation and more concentrated on the anion. The Mulliken analysis indicates that the fluorides of Li and Na are more covalent than the chlorides, and the covalent character is stronger for DFT (LDFT in particular) than for the HF method. This is not consistent with the ionic character scale given in Table 2 which predicts a very strong ionic behavior for the fluorides of these two cations. However, if we compare LiCl with LiBr and NaCl with NaBr we find, in both cases, a reduction in the charge at all levels of theory which can be interpreted as an increase in the covalent character of the solid. These variations of the net charge give a picture of the ionic character more complex than would be given by a simple ionic model based on the values in Table 2, and in general, the DFT results follow the path shown by the HF calculations.

The bond population q(M−X) is usually positive, and q(X−X) is negligible except for the lithium halides LiCl, LiBr, and LiI which exhibit negative values along the X−X distance; the size of this effect is always larger with the HF method. The maximum value of this negative population is found for LiBr (−0.077e, −0.040e, and −0.035e for HF, NLDFT and LDFT, respectively). From F^- to Br^-, it is the increase of the size of the anion that induces the increase of the repulsion (the population becomes more negative), but this feature cannot explain the drop of q(X−X) for the most diffuse anion. However, the iodide is also the most polarizable anion, and for this reason Li^+ tends to drive the anion charge more efficiently along the direction Li−X, as shown by q(Li−I) values.

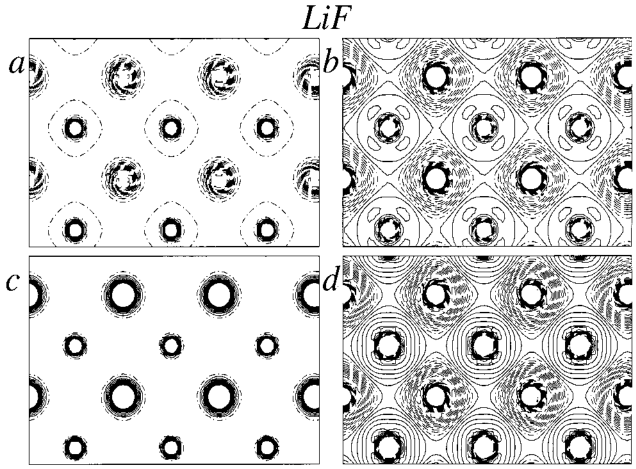

Figure 4. Differential maps of [001] plane of LiF. Isoline curves are separated by 0.0007 e/bohr^3. (a) DFT with HF exchange and Perdew−Wang correlation minus HF density, (b) DFT with Becke exchange and Perdew−Wang correlation minus HF density, (c) DFT with HF exchange and Volsko−Wilk−Nusair correlation minus HF density, (d) DFT with Slater exchange and Volsko−Wilk−Nusair correlation minus HF density.

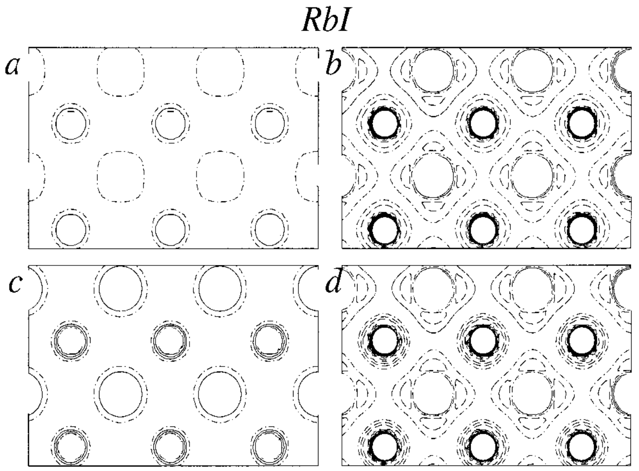

Figure 5. Maps of [001] plane of RbI. See Figure 4 caption.

Density Maps. The total density of the crystal at different levels of theory can be used not only to obtain more information about the properties of the crystals, but also to analyze any differences between the different computational methods that were used. The total density, along a particular crystallographic plane, gives a relatively small amount of information. The function obtained as the difference of the total density of the crystal and the density of the array of noninteracting ions is more interesting because it displays how covalent a particular bond is. The section along the plane [001] of the difference between the total HF density (ρ_{HF}) and densities calculated at various DFT levels are given in Figures 4 and 5, for LiF and RbI. Figure 4a and b show, for LiF, the NLDFT density obtained by using exact (HF) exchange and the Perdew−Wang correlation functional *minus* the HF density ($\Delta\rho_{NL*-HF} = \rho_{PW-B} - \rho_{HF}$) (a), and the "true" NLDFT density obtained when Perdew−Wang correlation and Becke exchange functionals are used in the Kohn−Sham equations *minus* the HF density ($\Delta\rho_{NL-HF} = \rho_{PW-B} - \rho_{HF}$) (b). Figure 4c and d are $\Delta\rho_{LDA*-HF} = \rho_{VWN-HF} - \rho_{HF}$ (c) and $\Delta\rho_{LDA-HF} = \rho_{VWN-S} - \rho_{HF}$ (d), where ρ_{VWN-S} represents the total DFT density obtained by using the Volsko−Wilk−Nusair correlation and Slater exchange functionals and ρ_{VWN-HF} is the density when the local exchange is replaced by the exact HF exchange. Examination of the plot $\rho_{HF} - \rho_{HF}^{ion}$ (not shown) indicates that, with respect to a pure ionic representation of the crystal, the HF calculation for the periodic system tends to add density on the cations and deplete the anions, i.e., it introduces covalency and reduces the difference in the positive and negative charges. Figure 4d shows that the LDFT method, with respect to Hartree−Fock, reduces the ionicity just as expected from the Mulliken populations. The cations display additional positive (solid lines) isolines around the Li^+ sites and additional negative (dashed lines) isolines surround the anion. If the self-consistent calculations are performed with the local correlation functional and exact (HF) exchange (Figure 4c), the result (in comparison with the HF) is a concentration of the electron density in the core region of the ions, but the difference is much smaller than if the Slater exchange is used. The NLDFT plots (Figure 4a and b) show the same features as seen in the LDFT difference density plots but the differences from the HF plots are smaller. If HF exchange and the nonlocal correlation functional are used (Figure 4a), the density in the inner region of Li^+ increases with respect to the HF density just as found in the LDFT plots, but there is a depletion of density around the anion. Clearly the main difference between the HF and DFT densities is due to the treatment of exchange.

The sections of the differential densities of RbI (the largest ions studied) are shown in Figure 5 and the main feature is the shrinking of the density around the iodides, induced by the electrostatic field created by the cations $(\Delta\rho\text{ion})_{HHF}$. However, in this case the charge on Rb^+ appears to be depleted. The nonlocal and the local functionals (differential maps b and d in Figure 5) slightly reduce the small polarization on I^- and increase the shrinking of the density around both the ions. This effect is much smaller when exact exchange and either correlation functional is used (differential maps a and c of Figure 5). It is useful to note that for RbI, which has the largest unit cell treated in this study, the density differences between the various methods are the smallest that we have observed, consistent with the least interactions between the cations and anions (The various plots for LiI and RbF are given as Supporting Information).

The density plots clearly show that it is the treatment of the exchange which differentiates the periodic HF and the periodic DFT calculations. The analysis of the (001) differential density maps for other alkali halides (for LiI and RbF, see Supporting Information) show that the effect is most pronounced when the lattice constant is smallest with large transfer of electron density from the anion to the cation. The gradient corrections to the functionals moderate this transfer of electron density, making the system more ionic. Increasing the interatomic distances (and changing the polarizability of the anion), dramatically reduces the difference between full DFT and HF as found for LiI. The two rubidium halides show similar trends to the two lithium halides but the differences are not as pronounced, i.e., there is less differentiation between the fluoride and the iodide for rubidium. Finally we note that the gradient correlation corrections do little to change the HF results.

Lattice Energies. The lattice energies (E_L) calculated with the DZVP basis sets for the alkali halides studied in this work are given in Table 6. The E_L are computed as the difference between the total energy per formula unit *minus* the sum of the total energies of the isolated anion and cation, evaluated at the same level of theory with respect to the periodic calculations. The HF and NLDFT methods underestimate the lattice energies whereas the LDFT method overestimates them. This is consistent with the well-known trend for LDFT to give

TABLE 6: Experimental[40] and Calculated Lattice Energies (kJ/mol), for the Alkali Halides at Hartree−Fock (HF), LDFT, and NLDFT Levels with the Optimized DZVP Basis Sets. Values in Parentheses Are Percentage Errors

		lattice energies			
		F	Cl	Br	I
Li	exptl	1036	835	807	757
	HF	1023.6(−1.2)	817.1(−2.1)	790.5(−2.0)	701.7(−7.3)
	NLDFT	1011.9(−2.3)	806.1(−3.6)	795.1(−1.5)	642.3(−15.2)
	LDFT	1106.2(+6.8)	885.4(+6.0)	882.7(+9.4)	746.2(+1.4)
Na	exptl	923	786	747	704
	HF	939.5(+1.8)	754.5(−4.0)	740.5(−0.9)	658.3(−6.5)
	NLDFT	905.5(−1.9)	737.9(−6.1)	738.6(−1.1)	602.7(−14.4)
	LDFT	980.1(+6.1)	822.3(+4.6)	826.1(+10.6)	698.8(−0.7)
K	exptl	821	715	682	649
	HF	805.2(−1.9)	666.5(−6.8)	662.2(−2.9)	592.6(−8.7)
	NLDFT	785.0(−4.4)	647.9(−9.4)	665.7(−2.4)	579.1(−10.8)
	LDFT	867.8(+5.7)	730.6(+2.2)	749.0(+9.8)	667.6(+2.9)
Rb	exptl	785	689	660	630
	HF	682.5(−13.1)	637.5(−7.5)	638.2(−3.3)	563.8(−10.5)
	NLDFT	679.9(−13.4)	618.2(−10.3)	640.1(−3.0)	518.7(−17.7)
	LDFT	804.0(+2.4)	716.9(+3.9)	738.6(+11.8)	624.2(−0.9)

overbinding. Despite the linear correlation between the Δa_o% and the lattice energies errors found at the HF level[19] for the Li, Na, and K fluorides and chlorides, our results do not show any particular trend as a function of the size of the anion or the cation. However, the HF and NLDFT evaluations are, in some way, correlated; for a particular cation, when the size of the anion increases both the methods show the same behavior. If the HF error increases (decreases), the NLDFT increases (decreases), but the size of the fluctuation can be quite different. For the potassium halides, for example, the HF error for the KF lattice energy is −1.9%, but −4.4% for NLDFT. The error increases for KCl (−6.8% and −9.4% at the HF and NLDFT level, respectively) then decreases for KBr (−2.9% and −2.4%); NLDFT gives a larger underestimation (−15.2%) for KI as compared to the HF error of −7.3%. The LDFT method exhibits a different behavior but its errors can be correlated with the HF and NLDFT ΔE_L%. The compounds which have smaller (larger) underestimation of E_L at the HF and NLDFT level, show larger (smaller) overestimation at LDFT level. We note that the HF and NLDFT errors are largest for the iodides and the chlorides whereas the errors are much smaller for the fluorides and bromides.

4. Conclusions

The HF and NLDFT methods tend to overestimate the lattice constants by a few percent. In general NLDFT predicts more accurate lattice constants than HF. The LDFT method always predicts lattice constants that are too short although the absolute error is usually smallest at this level. The bulk moduli are usually predicted to be too low at the HF and NLDFT levels consistent with the longer lattice constants and the LDFT bulk moduli are too large as expected from the shorter lattice constant as compared to experiment. Surprisingly, the largest absolute error in the bulk moduli is found at the LDFT level even though the smallest absolute error in the lattice constant is found at this level. The HF and NLDFT lattice energies are usually too low and the LDFT values are too high; the latter is consistent with the well-known tendency of LDFT to predict overbinding. The predicted lattice energies do not show a periodic trend. The iodides are the most difficult to calculate, followed by the chlorides.

The results show that the HF-derived solid state basis sets can be used in the solid state DFT calculations without a significant loss in accuracy. Obviously, as in molecular calculations, improvements in the one-particle space does lead to improved agreement with experiment. The difference density maps clearly show that it is the different treatment of exchange which differentiates the HF and DFT results. The treatment of correlation does little to change the density maps of these very ionic systems. The gradient corrections at the DFT level do lead to smaller density differences with respect to the HF density.

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Supporting Information Available: Explanation of the use of DFT basis sets, tables of DZVP basis sets for cations, and maps of the [001] plane for LiI and RbF (7 pages). Ordering information is given on any current masthead page.

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