Direct determination of self-consistent total energies and charge densities of solids: A study of the cohesive properties of the alkali halides

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A recently proposed method for directly determining the self-consistent total energies and charge densities of solids is used to study the cohesive properties of all the alkali halides. The calculated lattice parameter, bulk modulus, and dissociation energy of each compound are reported and compared with the corresponding experimental data. The results have a good accuracy and their analysis gives some insights on possible improvements of the approximations that we have used. The relativistic contributions to the various properties have been evaluated by performing fully relativistic calculations for the heaviest compounds: The most relevant effect is an increase of the dissociation energies of the cesium halides which, for CsI, amounts to 7% of the experimental value.

I. INTRODUCTION

In a recent paper[1] we have proposed a method of determining the self-consistent charge densities and total energies of molecules or solids without the prior need to derive the wave functions of these systems. This method is based on the second theorem of Hohenberg and Kohn,[2] which states that the ground-state density of an electronic system can be found by minimizing the following density functional:

$$E_v[\rho]=T_{ni}[\rho]+J[\rho]+E_{xc}[\rho]+\int V_{nuc}(\mathbf{r})\rho(\mathbf{r})d^3r , \quad (1)$$

where $T_{ni}[\rho]$ is the kinetic energy of a fictitious system of noninteracting electrons having the same ground-state charge density as the real system,[3,4] $J[\rho]$ is the electrostatic energy, $V_{nuc}(\mathbf{r})$ is the external potential (in most cases the Coulombic potential of a static distribution of nuclear charges), and $E_{xc}[\rho]$ is the exchange-correlation energy functional. The latter is defined as follows:

$$E_{xc}[\rho]=T_i[\rho]-T_{ni}[\rho]+V_{ee}[\rho]-J[\rho] , \quad (2)$$

where $T_i[\rho]$ and $V_{ee}[\rho]$ are, respectively, the kinetic energy of the real system and the total interaction energy of the electrons. The existence of the two functionals $T_i[\rho]$ and $V_{ee}[\rho]$ is guaranteed by the first Hohenberg and Kohn theorem,[2] while the particular definition of $T_{ni}[\rho]$ allows one to find the charge density minimizing $E_v[\rho]$ by solving the following one-electron equation:[3]

$$[-\tfrac{1}{2}\nabla^2+V_{eff}(\mathbf{r})]\psi_i(\mathbf{r})=\varepsilon_i\psi_i(\mathbf{r}) , \quad (3)$$

with the effective potential

$$V_{eff}(\mathbf{r})=V_{nuc}(\mathbf{r})+\frac{\delta J}{\delta\rho}+\frac{\delta E_{xc}}{\delta\rho} , \quad (4)$$

and then summing the square of the N lowest orbitals

$$\rho(\mathbf{r})=\sum_{i=1}^{N}|\psi_i(\mathbf{r})|^2 , \quad (5)$$

N being the number of electrons of the system.

This is the standard Kohn and Sham[3] method for solving the electronic-structure problem of a system. Just one approximation is required: as the explicit form of $E_{xc}[\rho]$ is unknown, one has to replace it by some approximate functional $E_{xc}^{approx}[\rho]$. Thus, in practice, one looks for the minimum of a given $E_v^{approx}[\rho]$.

This method requires a complete solution of the one-electron problem for the system: the computational effort to do this increases roughly as N_{at}^3, the third power of the number of atoms in the molecule or in the unitary cell of the crystal.

In Ref. 1, we have shown that a simpler method can be obtained by proceeding in the following way. (i) Instead of solving Eq. (3), one directly looks for the charge density minimizing E_v^{approx}; (ii) in order to do this, one rewrites the total charge density as the superposition of the charge densities of localized subsystems and (iii) one splits the total kinetic energy in the sum of two contributions: the sum of the kinetic energies of the subsystems and the change of total kinetic energy due to their interaction. Finally (iv) one treats the first of these contributions exactly and uses an approximation for the second one. The resulting method is less accurate than the Kohn and Sham one, but it has the advantage of linearly scaling with N_{at}.

In the earlier paper[1] we have reported some preliminary result obtained by such a method; here, we present the results of a systematic application of it: a study of the cohesive properties of all the alkali halide crystals.

The paper is organized as follows: in Sec. II, the features of the method will be described; in Sec. III, the analogies and the differences with other similar methods will be analyzed; in Sec. IV, the approximations we have used in the actual calculations will be discussed as well as our choice of experimental data; the detailed comparison between experimental and theoretical results will be done in Sec. V; finally, some conclusions will be drawn in Sec. VI. Note that the formalism will be described for the case of a crystal, a molecule being an obvious particular case.

II. DESCRIPTION OF THE METHOD

Let us consider a nonmagnetic crystal and indicate with $\mathbf{R}_k$ the points of its Bravais lattice. Let τ_j indicate some points within the primitive cell. Suppose we partition the crystal in subsystems localized around the points $\mathbf{R}_k + \tau_j$. We will indicate with $\rho_j(\mathbf{r} - \mathbf{R}_k - \tau_j)$ the electronic density of the kj subsystem and with $V_j^{\text{nuc}}(\mathbf{r} - \mathbf{R}_k - \tau_j)$ its contribution to the nuclear electrostatic potential:

$$\rho_{\text{tot}}(\mathbf{r}) = \sum_{j,k} \rho_j(\mathbf{r} - \mathbf{R}_k - \tau_j) , \tag{6}$$

$$V_{\text{nuc}}(\mathbf{r}) = \sum_{j,k} V_j^{\text{nuc}}(\mathbf{r} - \mathbf{R}_k - \tau_j) . \tag{7}$$

Note that zero, one or several nuclear charges can be associated to each point, the choice of the partition depending upon the nature of the crystal to be studied.

The electronic densities $\rho_j(\mathbf{r} - \mathbf{R}_k - \tau_j)$ can be written in terms of one-electron wave functions as follows:

$$\rho_j(\mathbf{r} - \mathbf{R}_k - \tau_j) = \sum_i 2n_{ij} |\psi_{ij}(\mathbf{r} - \mathbf{R}_k - \tau_j)|^2 , \tag{8}$$

where the ψ_{ij} are assumed to be normalized and to decrease exponentially as $\mathbf{r}$ tends to infinite. The coefficients n_{ij} are electronic occupation numbers. They must satisfy the condition $0 \le n_{ij} \le 1$, but, otherwise, they are not restricted in any other way. In particular, they can be fractionary and the integral of ρ_j does not need to be an integer number.

Using the ψ_{ij}, we can associate to each subsystem a kinetic energy T defined by

$$T[n_{ij}, \psi_{ij}] = \sum_i 2n_{ij} \langle \psi_{ij} | (-\tfrac{1}{2}\nabla^2) | \psi_{ij} \rangle . \tag{9}$$

We can also write the functional $T_{\text{ni}}[\rho]$ as the sum of two terms:

$$T_{\text{ni}}[\rho] = \sum_{j,k} T[n_{ij}, \psi_{ij}] + \left[T_{\text{ni}}[\rho] - \sum_{j,k} T[n_{ij}, \psi_{ij}] \right] . \tag{10}$$

The first of these terms is the sum of the kinetic energies of the subsystems, while the second one is the contribution of the interaction between the subsystems to the kinetic energy of the crystal.

If $T^{\text{approx}}[\rho]$ is an approximate expression of the functional $T_{\text{ni}}[\rho]$, we replace the exact functional $E_v[\rho]$ with the following:

$$\begin{aligned}
E_v^{\text{approx}}[n_{ij}, \psi_{ij}] &= \sum_{j,k} T[n_{ij}, \psi_{ij}] \\
&+ \left[T^{\text{approx}}[\rho] - \sum_{j,k} T^{\text{approx}}[\rho_{jk}] \right] \\
&+ J[\rho] + E_{\text{xc}}^{\text{approx}}[\rho] \\
&+ \int V_{\text{nuc}}(\mathbf{r})\rho(\mathbf{r})d^3r ,
\end{aligned} \tag{11}$$

where we have used ρ_{jk} as an abbreviation of $\rho_j(\mathbf{r} - \mathbf{R}_k - \tau_j)$. We will look for the minimum of this functional with respect to n_{ij} and to ψ_{ij}.

By varying $E_v^{\text{approx}}[n_{ij}, \psi_{ij}]$ with respect to ψ_{ij}, under the normalization condition, and for a fixed choice of n_{ij}, one obtains the following equation:

$$\left[-\frac{1}{2}\nabla^2 + V_{\text{nuc}} + \frac{\delta J}{\delta\rho} + \frac{\delta E_{\text{xc}}^{\text{approx}}}{\delta\rho} + \frac{\delta T^{\text{approx}}}{\delta\rho} - \frac{\delta T^{\text{approx}}}{\delta\rho_{jk}} \right] \psi_{ij}(\mathbf{r} - \mathbf{R}_k - \tau_j) = \varepsilon_{ij}\psi_{ij}(\mathbf{r} - \mathbf{R}_k - \tau_j) . \tag{12}$$

Furthermore, we have proved[1] that the eigenvalues ε_{ij} are related to the derivative of E_v^{approx} with respect to n_{ij} in the following manner:

$$\varepsilon_{ij} = \frac{1}{2}\frac{1}{N_c}\frac{\partial E_v^{\text{approx}}}{\partial n_{ij}} , \tag{13}$$

where N_c is the number of primitive cells in the crystal. Thus, in order to minimize the total energy, one has to solve Eq. (12) for all the subsystems belonging to a given primitive cell of the crystal and to fill up the levels following the Fermi statistics. Of course, one has to proceed iteratively until the self-consistent total charge density is found. In doing this, the problem arises of calculating the effective potential entering in Eq. (12). In particular,

one has to perform two kinds of lattice sum. The first one, which enters in the kinetic and the exchange-correlation contributions to the potential, is the sum of the densities of the subsystems: as these charge densities decrease exponentially, one can limit the sum to a finite number of terms and the consequent error on the potential will be not negligible only in a region where the ψ_{ij} are exceedingly small. The second one is the sum of the electrostatic potentials generated by the subsystems, which are typically long-range contributions. Let us discuss these lattice sums for the particular case which is of interest in this paper: the case of subsystems spherically symmetric around the points $\mathbf{R}_k + \tau_j$. The electrostatic potential can then be written as the sum of a long-range point-ion potential and a short-range contribution:

$$\begin{aligned}
V_{\text{nuc}}(\mathbf{r}) + \frac{\delta J}{\delta\rho} &= \sum_{j,k} \left[V_j^{\text{nuc}}(\mathbf{r} - \mathbf{R}_k - \tau_j) + \int \frac{\rho_j(\mathbf{r}' - \mathbf{R}_k - \tau_j)}{|\mathbf{r} - \mathbf{r}'|} d^3r' \right] \\
&= \sum_{j,k} \frac{I_j}{|\mathbf{r} - \mathbf{R}_k - \tau_j|} + \sum_{j,k} \left[V_j^{\text{nuc}}(\mathbf{r} - \mathbf{R}_k - \tau_j) - \frac{I_j}{|\mathbf{r} - \mathbf{R}_k - \tau_j|} + \int \frac{\rho_j(\mathbf{r}' - \mathbf{R}_k - \tau_j)}{|\mathbf{r} - \mathbf{r}'|} d^3r' \right] \\
&= \sum_{j,k} V_j^{\text{ip}}(\mathbf{r} - \mathbf{R}_k - \tau_j) + \sum_{j,k} V_j^{\text{sr}}(\mathbf{r} - \mathbf{R}_k - \tau_j) ,
\end{aligned} \tag{14}$$

where the I_j are the ionic charges of the subsystems. Now, the lattice sums can be easily performed: the point-ion contributions can be summed using standard techniques, while the short-range terms need only to be taken into account up to finite order of neighbors.

Finally, the potential entering in Eq. (12) can be split in an "internal" contribution

$$V_j^{\text{int}}(\mathbf{r}-\mathbf{R}_k-\boldsymbol{\tau}_j)=V_j^{\text{ip}}(\mathbf{r}-\mathbf{R}_k-\boldsymbol{\tau}_j)+V_j^{\text{sr}}(\mathbf{r}-\mathbf{R}_k-\boldsymbol{\tau}_j)+\frac{\delta E_{\text{xc}}^{\text{approx}}}{\delta\rho_{jk}}$$

$$=V_j^{\text{nuc}}(\mathbf{r}-\mathbf{R}_k-\boldsymbol{\tau}_j)+\int\frac{\rho_j(\mathbf{r}'-\mathbf{R}_k-\boldsymbol{\tau}_j)}{|\mathbf{r}-\mathbf{r}'|}d^3r'+\frac{\delta E_{\text{xc}}}{\delta\rho_{jk}}\ , \tag{15}$$

and a "crystalline" potential:

$$V_j^{\text{cryst}}(\mathbf{r}-\mathbf{R}_k-\boldsymbol{\tau}_j)=\sum_{j',k'}{}'V_{j'}^{\text{ip}}(\mathbf{r}-\mathbf{R}_{k'}-\boldsymbol{\tau}_{j'})+\sum_{j',k'}{}'V_{j'}^{\text{sr}}(\mathbf{r}-\mathbf{R}_{k'}-\boldsymbol{\tau}_{j'})+\frac{\delta E_{\text{xc}}^{\text{approx}}}{\delta\rho}-\frac{\delta E_{\text{xc}}^{\text{approx}}}{\delta\rho_{jk}}+\frac{\delta T^{\text{approx}}}{\delta\rho}-\frac{\delta T^{\text{approx}}}{\delta\rho_{jk}} \tag{16}$$

where the prime means that the term corresponding to $j'k'=jk$ is not included in the sums.

III. COMPARISON WITH OTHER RELATED METHODS

The first attempt of describing the interaction of two systems starting from the superposition of their charge densities was made by Gordon and Kim.[5] These authors proposed the following interaction potential V for two closed shells atoms or ions having charge densities ρ_1 and ρ_2:

$$V=V_{\text{els}}+T^{\text{approx}}[\rho_1+\rho_2]-T^{\text{approx}}[\rho_1]-T^{\text{approx}}[\rho_2]$$

$$+E_{\text{xc}}^{\text{approx}}[\rho_1+\rho_2]-E_{\text{xc}}^{\text{approx}}[\rho_1]-E_{\text{xc}}^{\text{approx}}[\rho_2]\ , \tag{17}$$

where V_{els} is the electrostatic interaction of the two atoms. The densities ρ_1 and ρ_2 were obtained from free-atom (ion) calculations and T^{approx} and $E_{\text{xc}}^{\text{approx}}$ were taken from the homogeneous gas theory.

This approach was soon applied to solids[6] and then refined in several different ways. In particular, modified electron gas expressions for T^{approx} and $E_{\text{xc}}^{\text{approx}}$ were used;[7] the so-called Watson sphere was introduced in order to approximately take into account the effects of the crystalline field;[7] many-body effects were also included.[8] Successively, other authors further refined the model by coupling the radius of the Watson sphere with the Madelung potential.[9]

Our method is similar to the most accurate versions of this theory: if one partitions the crystal into atomic subsystems, the interactions of the latter are described in the same way as in the Gordon-Kim theory with, of course, the many-body and the crystalline-field effects taken into account. However, our method has the advantage of being completely self-consistent: no assumption for the charge densities of the subsystems, for the crystalline field or for the charge transfer between the subsystems is required.

The crystalline potential given in Eq. (16) was used by Johnson, Subbaswamy, and Senatore in a study of the hyperpolarizabilities of the alkali halides.[10] These authors were mainly concerned in taking into account the solid-state effects on the hyperpolarizabilities and they did not derive variationally the potential. Furthermore, they assumed unitary ionic charges, while, in our theory, the charge transfer is a result of the calculation.

In order to simplify the problem of calculating the interaction energy of two weakly interacting fragments, Harris proposed[11] to solve the Kohn and Sham equation for the overall system with a one-electron potential obtained by superposing the unperturbed densities of the two fragments. Furthermore, he was able to show that the total energy could be calculated from the one-electron energies and from the unperturbed densities, with errors of the second order in the changes of total density and of total effective potential produced by the interaction of the two fragments. The Harris method has the main advantage of treating the interaction contribution to the kinetic energy exactly; on the other hand, it has the drawback of neglecting the effects of self-consistency.

Very recently, Yang has proposed[12] a method which is very close to ours under several aspects: in order to derive the charge density and the total energy of a complex system, Yang partitions it into subsystems and solves a Kohn-Sham equation for each subsystem. The effective potential which enters in these equations is derived from the total charge density and the latter is obtained by superposing the charge densities of the subsystems. The charge transfer between the subsystems is determined by assuming that there is a common Fermi level for the subsystems.

There are several minor differences between Yang's and our method (for example, the way of partitioning the electronic density of the system) and their applications have been made by using quite different techniques. There is also a basic difference, because Yang has conceived his method as an approximate way of solving the Kohn and Sham equation, while our method is based on the Hohenberg-Kohn variational principle. A consequence of this is that in our theory the existence of a common Fermi level for the subsystems follows from Eq. (13), while in Yang's theory that is an assumption of the method. In practice, however, the main difference is in the treatment of the subsystem interactions: we have a kinetic contribution to these interactions [the term in parentheses in Eq. (10)], a contribution that is not present in Yang's theory.

Finally, we would like to mention that a quite different method of calculating the properties of solids which

scales linearly with N_{at} has also been proposed by Baroni and Giannozzi.[13] We refer to the original paper for details.

IV. THEORETICAL RESULTS AND EXPERIMENTAL DATA

All the results reported in this paper have been obtained using the general theory of Sec. II with the following particular choices: (i) The local approximation has been used for the kinetic, exchange and correlation energy functionals. For the latter, we have used the Perdew and Zunger[14] parametrization of the Ceperley and Alder[15] Monte Carlo data for the homogeneous gas; (ii) the crystals have been partitioned in atomiclike subsystems; (iii) the short-range contributions to the potential have been taken into account up to fourth order of neighbors. Beyond this order ions have been considered as point charges; (iv) the potential has been spherically averaged around each site as explained in Ref. 1.

For all the alkali-halide crystals and for both the B1 (NaCl) and B2 (CsCl) lattice structures, we have calculated the total energy per primitive cell corresponding to several lattice parameters (12–16) disposed in an approximatively symmetric way around the supposed equilibrium position. A spacement of 0.05 Å between two contiguous lattice parameters has been taken, with the exception of the two last values on each side, for which 0.1 Å has been chosen. The results have been fitted by second, third, and fourth degree polynomials and the best fits have been repeated reducing progressively (and symmetrically) the number of calculated values. By proceeding in this way, we have noted no appreciable variation of the equilibrium lattice parameters and of the minimal total energies. This is not the case for the bulk moduli, which

are more sensitive quantities. In general, however, the results obtained by using a fourth degree polynomial are remarkably stable and those obtained by a third degree polynomial converge very quickly to the preceding ones. On the contrary, a second degree polynomial is rarely adequate. The bulk moduli reported in Table III are the most reliable values obtained from this analysis and all the results of meaningful best fits[16] are covered by considering a possible error of ±0.5 GPa on the calculated values.

The experimental lattice parameters reported in Table I are taken from the Landolt-Börnstein tables.[17] Only one remark about them is in order: the room-temperature values are not taken, in general, from the same paper where the temperature dependence has been studied. In some rare cases this gives rise to slight inconsistencies.[18]

We have found some inconsistency also in the experimental dissociation energies (referred to free atoms) reported in the literature: we think, in particular, of the case of NaCl, for which we have found 6.39 eV,[19] 6.8 eV,[20] and 6.6 eV.[21] The "experimental" dissociation energies reported in this paper (see Table II) have been evaluated by using the heat of formation data at 0 K for the compounds and for the free-atom gas compiled by Wagman et al.[22] When 0-K data were not available (LiBr and RbF), we have used the corresponding quantities at room temperature: this yields a negligible difference in the results.

The experimental bulk moduli are deduced from the measured elastic constants. In Table III, we have reported two kinds of data. First, the values calculated from the tables of room-temperature elastic constants reported in Landolt-Börnstein.[23] These are average values of the most reliable experimental data. Second, we have report-

TABLE I. Calculated and experimental (Ref. 17) lattice parameters in Å. The values in parentheses are the results of relativistic calculations.

		F	Cl	Br	I
Li	$T=298$ K	4.03	5.14	5.50	6.01
	$T=0$ K	4.01	5.11	5.46	5.95
	Calculated	4.05	5.08	5.44	5.93 (5.91)
Na	$T=298$ K	4.62	5.64	5.97	6.47
	$T=0$ K	4.61	5.60	5.93	6.41
	Calculated	4.76	5.75	6.10	6.60 (6.58)
K	$T=298$ K	5.34	6.29	6.60	7.07
	$T=0$ K	5.31	6.25	6.54	6.99
	Calculated	5.40	6.26	6.57	7.03 (7.01)
Rb	$T=298$ K	5.65	6.59[a]	6.89	7.34
	$T=0$ K	5.59	6.53	6.82	7.26
	Calculated	5.73	6.57	6.88 (6.87)	7.33 (7.31)
Cs	$T=298$ K	6.02[a]	4.12	4.30	4.57
	$T=0$ K			4.23[b]	4.51[b]
	Calculated	6.12 (6.10)	4.11 (4.10)	4.27 (4.26)	4.52 (4.50)

[a]Values that correspond to $T=293$ K.
[b]Values taken from Ref. 31.

TABLE II. Calculated and experimental (Ref. 22) dissociation energies (referred to free atoms) in eV. The values in parentheses are the results of relativistic calculations.

		F	Cl	Br	I
Li	$T=0$ K	8.8	7.1	6.5[a]	5.6
	Calculated	9.4	7.2	6.4	5.4 (5.5)
Na	$T=0$ K	7.8	6.6	6.0	5.2
	Calculated	8.0	6.3	5.6	4.7 (4.7)
K	$T=0$ K	7.6	6.7	6.2	5.4
	Calculated	8.0	6.6	6.0	5.1 (5.2)
Rb	$T=0$ K	7.4[a]	6.6	6.1	5.4
	Calculated	7.6	6.3	5.7 (5.8)	4.9 (5.1)
Cs	$T=0$ K	7.3	6.6		5.5
	Calculated	7.3 (7.7)	6.1 (6.4)	5.5 (5.8)	4.7 (5.1)

[a]Values that correspond to $T=298$ K.

TABLE III. Calculated and experimental bulk moduli in GPa. Second and third columns: experimental values at 4.2 and 300 K, respectively. Fourth column: average room-temperature values from the tables of Landolt-Börnstein (Ref. 23). Last column: calculated values.

	$T=4.2$ K	$T=300$ K	LB	Calc.
LiF	69.9[a]	64.9[a]	68.0	70.5
LiCl	35.4[b]	31.8[b]	31.0	35.2
LiBr	26.3[c]	25.7[c]	25.7	28.5
LiI			18.8	22.0
NaF	51.4[b]	48.5[b]	48.5	42.3
NaCl	26.6[b]	25.0[b]	24.9	22.8
NaBr	22.6[b]	19.9[b]	20.4	18.6
NaI	17.9[d]	16.1[d]	16.1	14.9
KF	34.2[b]	31.8[b]	31.7	31.3
KCl	19.7[e]	17.8[e]	18.1	18.9
KBr			15.2	16.3
KI	12.7[e]	12.0[e]	12.0	13.8
RbF	30.1[f]	28.0[f]	27.7	26.1
RbCl	18.7[b]	16.5[b]	16.3	16.6
RbBr	16.0[b]	13.8[b]	13.7	14.1
RbI	13.1[b]	10.8[b]	11.0	12.2
CsF			25.0	23.1
CsCl			18.2	18.8
CsBr	18.4[g]	15.6[g]	15.8	16.5
CsI	14.4[g]	12.5[g]	12.6	13.6

[a]Reference 26.
[b]Reference 25.
[c]Reference 27.
[d]Reference 28.
[e]Reference 29.
[f]Reference 30.
[g]Reference 31.

ed the bulk moduli at 4.2 K, when we have found experimental data at this temperature. In this latter case, we have also reported the values at 300 K taken from the same paper, in order to give a consistent indication of the change of the bulk moduli with the temperature. We recall that the elastic constants measured by different authors can differ substantially even at room temperature. For example, the bulk modulus of LiCl reported by Marshall, Pederson, and Dorris[24] is $B=28.7$ GPa, quite different from the value of 31.8 GPa reported in Table III and deduced from the elastic constants measured by Lewis, Lehoczky, and Briscoe.[25] More details on the different sets of measured elastic constants can be obtained by analyzing the figures on pages 109–215 of Ref. 23.

V. COMMENTS AND REMARKS

The theoretical and experimental lattice parameters of all the alkali halides in their experimental crystalline structure are compared in Table I. The theoretical values correspond to a *static* crystal, thus they should be slightly smaller than the $T=0$-K experimental values. This is the case of three lithium halides, while, in the other cases, they are larger. However, theoretical and experimental values at $T=0$ K differ, in most cases, by 1% or less and this seems to us a very satisfactory result. There are two notable exceptions: the sodium halides and the alkali fluorides. In the latter case the discrepancies are probably due to the use of the local-density approximation. As it is well known, most negative free ions are not stable in this approximation. Thus, when they are stabilized by the crystal field, as it is the case here, they have a charge density which is certainly too large and this effect is enhanced for the lightest ions. This is coherent with the results of Table I, and is a reason of the general trend of the calculated lattice parameters of being greater than the experimental ones. On the other hand, it is less clear why the results for the sodium halides are not as accurate as for the other alkali halides. In any case, the maximum discrepancy between the calculated and the $T=0$-K experimental values is not great: 3.3% for NaF.

The calculated and experimental dissociation energies are compared in Table II. The discrepancies are, in most cases, of a few percent and never exceed 10% (the error for CsI, 14.5%, can be reduced by performing relativistic calculations, see below). The main trends of the experimental data are correctly reproduced by the theoretical results: the decrease of the dissociation energy as the atomic number of the halide ion increases and the tendency of the potassium halides to have a greater dissociation energy than that of the corresponding sodium or rubidium halides.

The results for the bulk moduli are shown in Table III. Their analysis closely follows the one we have just made for the lattice parameters. A correct prediction should give bulk moduli slightly greater than the experimental values at 4.2 K (owing to zero-point effects). With a few exceptions, this is not correctly produced by our method. In most cases, the calculated values are between the $T=4.2$ K and the room-temperature experimental data.

TABLE IV. Differences between the equilibrium total energies per primitive cell of the $B2$ (CsCl) and $B1$ (NaCl) crystalline structures in millihartrees.

	F	Cl	Br	I
Li	26.6	20.6	21.4	18.5
Na	10.4	8.9	8.6	6.7
K	7.9	6.6	6.6	5.5
Rb	6.9	5.0	4.5	3.6
Cs	7.7	4.8	4.1	3.3

They differ from the former by roughly 10%, which is approximatively the accuracy of the standard band-structure calculations. Once more the results for the sodium halides are the worst: the discrepancies with respect to the low-temperature results are of 14–18 %.

We have also studied the relative stability of the $B1$ and $B2$ lattice structures. The differences between the equilibrium total energies per primitive cell of the two phases are reported in Table IV. As one can see, our results follow the trend that one expects: the relative stability of the $B1$ phase decreases in passing from one alkali halide to a contiguous and heavier one. This time, the anomalies come from the cesium halides: the decrease of the relative stability of the $B1$ phase becomes very small and, in the case of CsF, we even find an inversion of the general trend. As it appears from Table IV, all the alkali halides are predicted to be stable in the $B1$ phase, while experimentally CsCl, CsBr, and CsI are stable in the $B2$ phase.

We have checked the importance of the relativistic effects by performing fully relativistic calculations for the heaviest compounds. The results we have found for the lattice parameters and for the dissociation energies are reported in Tables I and II (the values in parentheses). In general, they are only slightly different from the nonrelativistic values and are in better agreement than the latter with the experimental data. The most remarkable effects we have found are on the dissociation energies of the cesium halides: 0.3 or 0.4 eV, that, for CsI, is 7% of the experimental dissociation energy and that reduces by 50% the error of our calculated value.

Finally, we have investigated the relativistic contributions to the bulk moduli and to the relative stability of the $B1$ and $B2$ phases. For this latter property we have not found any significant change in the case of CsI and so we have not extended the analysis to lighter compounds.

On the other hand, the relativistic effects seem to increase the bulk moduli. However, within the error which affects the calculated values, it is difficult to distinguish significantly the relativistic from the nonrelativistic values. In the case of CsI, for which the relativistic effects are enhanced, we have found a bulk modulus of 14.0 GPa.

VI. CONCLUSIONS

The results reported in this paper show that our method for the direct calculation of the total energies and the charge densities of solids enables one to predict, with good accuracy, the cohesive properties of highly ionic crystals such as the alkali halides. The analysis of the results for all the compounds of this class reveals that the approximations we have used slightly overestimates the repulsive interactions with respect to their attractive counterpart. This is made clear by the fact that we get lattice parameters that are too large and bulk moduli that are too small. In the preceding section, we have argued that this can be due, at least in part, to our use of the local-density approximation and, in particular, to the difficulties met by this approximation in treating the negative ions. One should be able to avoid this drawback by implementing the self-interaction correction, which has the main effect of reducing the extension of the negative-ion charge densities.

Another possible modification of the approximations we have used that should give rise to better results is to use an expression of the intersubsystems kinetic energy more accurate than the local-density one. We will investigate these two modifications in a future work.

ACKNOWLEDGMENTS

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