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# On the structural properties of NaCl: an *ab initio* study of the B1–B2 phase transition

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**Abstract.** The structural properties and the phase transition between the B1 (rock salt) and B2 (CsCl) phases of NaCl have been investigated at an *ab initio* level. Total energy curves, obtained with periodic Hartree–Fock (HF) calculations, have been corrected *a posteriori* by integrating the HF charge density according to the correlation-only density-functional-like formulae proposed by Colle and Salvetti (CS75) in 1975 and by Perdew in 1986 (P86) and 1991 (P91). The three functionals are ‘non-local’, containing terms that depend on the gradient of the electronic density. The correlation correction brings the HF data for the lattice energy (LE), lattice parameter ( $a_0$ ) and bulk modulus ( $B$ ) into good agreement with experiment, the best performance being obtained with the most recent functional, P91 (the percentage error is +0.3%, –0.5% and +5.6% respectively for LE,  $a_0$  and  $B$ ). The HF transition pressure (39.2 GPa) is slightly modified by the CS75 correction (37.2); P86 and P91 functionals reduce the computed value to 30.1 GPa and 28.9 GPa respectively, in better agreement with experiment (30 GPa).

## 1. Introduction

Alkali halides have been the object of a great number of studies. For a long time classical approaches based on Born-type semi-empirical formulae of various degrees of sophistication have been adopted for the calculation of the elastic and vibrational properties of ionic solids [1–3]. In the last decade many *ab initio* first-principles computational schemes have been implemented and applied to different classes of compounds. As regards ionics, NaCl can be considered the ‘test system’ to which nearly all such *ab initio* schemes have been applied in order to check the performance of the method. We report here the results of a Hartree–Fock (HF) and an HF plus correlation scheme, and our data are compared with the previous *ab initio* results in order to assess the limitations and merits of the different approaches.

The present *ab initio* all-electron results have been obtained with the CRYSTAL program [4]. CRYSTAL is an HF linear combination of atomic orbitals (LCAO) self-consistent field (SCF) program, and has been used previously to examine a range of other ionic compounds, including  $\text{Li}_2\text{O}$  [5, 6],  $\text{MgO}$  [7],  $\text{CaF}_2$  [8],  $\text{MgCl}_2$  [9] and  $\text{Al}_2\text{O}_3$  [10].

Extended Gaussian basis sets were adopted for the two ions: an  $s(8)$ ,  $sp(5)$ ,  $sp(1)$ ,  $sp(1)$  for Na and an  $s(8)$ ,  $sp(6)$ ,  $sp(3)$ ,  $sp(1)$ ,  $sp(1)$  for Cl, where the number in brackets is the number of contracted Gaussians used to represent the shell. The basis set for Na contains then 13 local functions (‘atomic orbitals’) and is the same as in the  $\text{Na}_2\text{O}$  study [6], apart from the exponent of the most diffuse  $sp$  shell ( $\alpha = 0.323 \text{ bohr}^{-2}$  in the present calculation). The Cl basis set contains 17 atomic orbitals and is the same as in [9] ( $\alpha = 0.125 \text{ bohr}^{-2}$  for the most diffuse shell in the present study).

From previous studies (see table 4 of [5]; the present basis set is equivalent to that indicated as (c) in the table) we can estimate that the error with respect to more complete basis sets is of the order of 2%, 0.2%, 2% for LE,  $a_0$  and  $B$ , respectively.

In the CRYSTAL code the accuracy of the 'direct-space' infinite Coulomb and exchange summations is controlled by five parameters, the details and effects of which are discussed elsewhere [4, 11]. High numerical accuracy was obtained using values of 6, 6, 6, 6, 14 for these parameters. The reciprocal-space integration was performed by sampling the Brillouin zone at a regular set of points [12] defined by a shrinking factor of eight (corresponding to 29  $k$  points).

The data referring to the B1 (rock salt) and B2 (CsCl) phases were established in a similar way, so that we can assume that the influence of the computational approximations and basis set incompleteness on the transition pressure is negligible.

It is well known that the HF energy and wavefunction are affected by the so-called 'correlation error' [13]. In density functional (DF) language the HF approach is an approximation in which the (unknown) exchange and correlation potential is represented only by the *exact* exchange potential. Among the many possibilities envisaged for correcting the 'correlation error' [14], by far the simplest consists in using density-functional-like correlation-only formulae, such as that proposed by Colle and Salvetti (CS75) [15–17] or, more recently, by Perdew in 1986 (P86) [18] and in 1991 (P91) [19, 20]. It is to be noted that these three functionals contain gradient terms, and should in principle be superior to the various 'local' functionals adopted in the papers to be discussed below.

The correction can be applied *a posteriori*, i.e. after the convergence with the HF Hamiltonian has been obtained. In this case one obtains a correction to the HF total energy by integrating the correlation function over the unit cell, the input being the HF charge density [18–20] or density matrix [15–17, 21]. Alternatively, one can add the correlation potential to the HF Hamiltonian through the SCF cycle, correcting in this way both the energy and the wavefunction, but this has not been done in the present work.

Application of the *a posteriori* scheme with the P86 functional [18] to a set of III–V and IV–IV semiconductors with the zinc-blend and diamond-type structure [22] gave quite encouraging results, the mean error on the binding energy for the 17 compounds considered being reduced from 40% to 2.6%. The same scheme is applied in the present study to NaCl.

## 2. Results and discussion

### 2.1. The B1 (rock salt) phase

The HF lattice energy data are reported in table 1 (calculation  $i$ ,  $j$ ,  $k$  and  $l$ ). The difference with respect to the experimental data is considerable: about –5% for LE, +4% for  $a_0$  and –20% for  $B$ . Such an error (which is a 'genuine' HF error, as the influence of the basis set limitations and of the numerical aspects of the calculation is small) is much greater than that found for a system containing lighter atoms, such as LiH [23], or with higher formal charge, such as MgO [7]. The reason is that in the first case interionic and intraionic correlation effects are much smaller, due to the smaller polarizability of the ions; in MgO the Coulomb effects prevail over the dispersion effects.

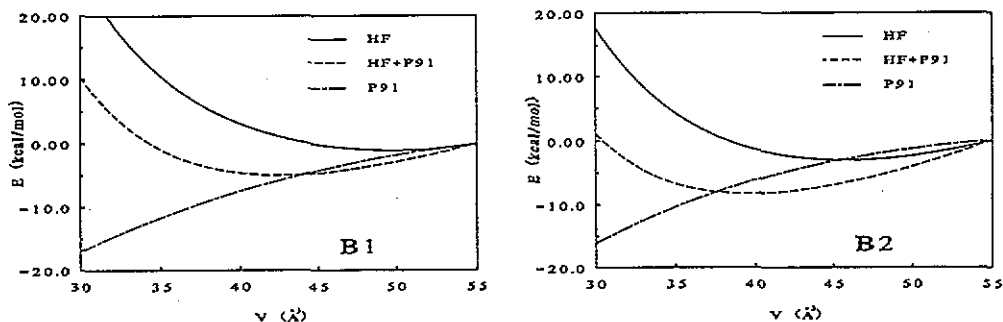
The HF plus correlation data are much closer to the experimental results; the three functionals, in spite of their quite different origin and functional form, correct in a similar way LE,  $a_0$  and  $B$ . It is interesting to note, however, that the error decreases systematically in going from the oldest functional (CS75) to the most recent one (P91) with the exception of the inversion between CS75 and P86 for  $a_0$ . Figure 1 shows the effect of correlation on the energy curve for the two phases.

**Table 1.** Lattice energy (LE in kcal mol<sup>-1</sup>), lattice constant ( $a_0$  in Å) and bulk modulus ( $B$  in GPa) for the B1 phase of NaCl, as resulting from local density functional (LDA) or Hartree-Fock (HF) calculations.  $D\%$  is the percentage difference with respect to the experimental data. The meaning of the acronyms specifying the different methods (the methods column) and functionals (the functionals column) is given in the text.

	Calc.	Method	Functional	LE	$D\%$	$a_0$	$D\%$	$B$	$D\%$
LDA	(a)	PS-PW	W			5.52	-0.9	31.2	+9.1
	(b)	FLAPW	HL	187.4*	-0.2	5.64	+1.3	30.4	+6.3
	(c)	LAPW	W			5.54	-0.5	28.7	+0.3
	(d)	LAPW	HL			5.47	-1.8	31.4	+9.8
	(e)	NUM	CA	203.2	+8.3	5.48	-1.6	31.5	+10.1
	(f)	ION	CA	180.9*	-3.6	5.75	+3.2	23.2	-18.9
	(g)	ASA+E	HL			5.49	-1.4	33.0	+15.8
HF	(h)	APII		167.9	-10.5	6.11	+9.7	14.8	-48.1
	(i)	LCAO		178.0	-5.2	5.80	+4.1	22.8	-20.0
HF + corr.	(j)	LCAO	CS75	192.5	+2.6	5.53	-0.7	32.5	+14.0
	(k)	LCAO	P86	190.1	+1.3	5.51	-1.1	32.1	+12.6
	(l)	LCAO	P91	188.3	+0.3	5.54	-0.5	30.1	+5.6
Expt				187.7 <sup>m</sup>		5.57 <sup>n,o</sup>		28.5 <sup>o</sup>	

\* Data obtained from the cohesive energy values evaluated with respect to the neutral atoms (binding energy) by adding the difference between the sodium ionization potential and the chlorine electron affinity [32].

- (a) From [24]. (h) From [31].  
 (b) From [25]. (i), (j), (k) and (l) This work.  
 (c) and (d) From [26]. (m) From [32].  
 (e) From [27]. (n) Static limit results from [33].  
 (f) From [28]. (o) Static limit results from [34].  
 (g) From [29].



**Figure 1.** Total energy of NaCl in the B1 and B2 phases as a function of the unit cell volume. Full curve: Hartree-Fock results. Chain curve: correlation contribution evaluated by using Perdew 1991 functional (P91). Broken curve: Hartree-Fock plus P91 correction. The curves have been shifted so as to coincide at the extreme right point, where the correlation energy is 720.4 and 722.2 kcal mol<sup>-1</sup> for the B1 and B2 phases, respectively.

It is of some interest to compare the present results with the *ab initio* calculations published in recent years [24–30] and obtained mostly within the local density approximation (LDA).

The results obtained by te Velde and Baerends [27] (calculation (e) in table 1) with a fully numerical scheme, by Feldman and co-workers [26] (calculation (d)) with a linear augmented-plane-wave (LAPW) program, and by Rodriguez and Methfessel [29] (calculation (g)) with the ASA+E version of the LMTO formalism, are very similar to each other, the error

with respect to experiment ranging from  $-1.4\%$  to  $-1.8\%$  for  $a_0$  and from  $+10\%$  ((e) and (d)) to  $+16\%$  ((g)) for  $B$ .

The full-potential linearized augmented-plane-wave (FLAPW) calculation of Jansen and Freeman ([25], calculation (b)) produces a lattice parameter 3% longer than those obtained in (d), (e), and (g). Feldman and co-workers attribute the disagreement to numerical inaccuracies in the Jansen and Freeman resolution of the secular equation (see p 6397 of [26]).

Calculations (c) and (d), performed with the same LAPW code and basis set by Feldman and co-workers [26], show that the Wigner functional (W) [35] produces a lattice parameter longer by 1.3% and a bulk modulus smaller by 9.5% than those obtained with the more recent Hedin and Lundqvist (HL) [36] (or Ceperley and Alder (CA) [37]) functional.

The plane-wave (PW) pseudopotential (PS) calculation (a) [24] performed by Froyen and Cohen gives a lattice parameter quite close to (c) (in both cases the W functional was used), whereas the bulk modulus is 10% larger. Feldman and co-workers "... tentatively attribute the difference ... to basis set limitations" of the PW-PS scheme (p 6397 of [26]).

The (f) calculation [28] is an interesting attempt for a 'direct' solution for the charge density and total energy of the system, without going through the determination of the Bloch states. Many approximations have however been introduced (such as spherical charge density in the 'atomic spheres', local density approximation for the 'interatomic' kinetic energy terms) which are probably responsible for the great differences with respect to the (e) calculation, performed using the same CA exchange-correlation functional.

Among the LDA based calculations the study by Bukowinski and Aidun [30] should also be mentioned, who used the APW scheme with a Lundqvist-Lundqvist [38] exchange-correlation functional. The room temperature (RT) data, obtained correcting the *ab initio* potential-energy curve for the zero-point and temperature effects with model calculations, are in perfect agreement with the RT experimental results, in spite of the use of the *muffin tin* approximation in the APW scheme.

In summary, it turns out that accurate LDA calculations with 'modern' exchange-correlation functionals (such as HL and CA) underestimate the lattice parameter by about 1.6%, and overestimate the bulk modulus by about 10%. At the moment it is difficult to say whether gradient-corrected functionals, such as those proposed recently by Perdew [18-20], Becke [39], Levy [40] and Lee, Yang and Parr [41], would improve the agreement with respect to experiment; in a recent paper García and co-workers [42] claim that "... Gradient-Corrected schemes do not provide a consistent and unequivocal improvement over the LDA in the calculated structural properties of crystalline solids".

As regards the lattice energy data, only in a few cases has such a quantity been evaluated. The te Velde and Baerends [27] LE overestimation of about 8% seems in line with the general trend of the LDA results (see for example the comments in [43]). The gradient-corrected functionals [15-21] in general provide better formation energies.

In the *ab initio* perturbed-ion (API) method due to Pueyo and co-workers [31] it is assumed that the crystalline electronic density can be obtained by solving separately the Schrödinger equation for the cation and subsequently for the anion in the crystalline field generated by the 'other' ions. At each stage of this self-consistent 'embedded-ion' process, a projection operator enforces the cluster (single ion, in this case) lattice orthogonality. A HF Hamiltonian and Slater basis functions are used. The very large difference between the present and API Hartree-Fock results can hardly be attributed to basis set differences. Some weakness in the API formal scheme, or inaccuracies in its implementation may be responsible for the discrepancies between the two sets.

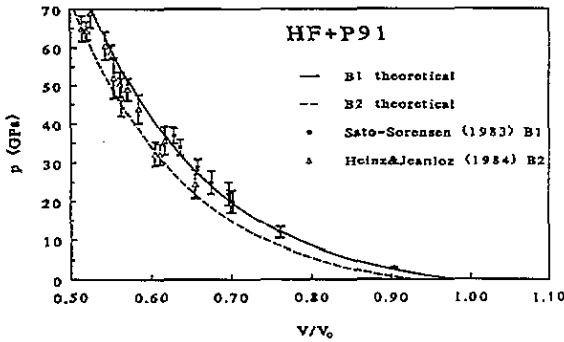


Figure 2. Calculated room-temperature equation of state. The figure reports the HF data corrected with the Perdew 1991 functional. The volume is normalized to the experimental volume  $V_c$ , measured at room temperature and  $p = 0$ , equal to  $44.86 \text{ \AA}^3$ .

Table 2. Transition pressures  $P_t$  (in GPa) and transition volumes (in  $\text{\AA}^3$ ) for the B1–B2 phase transformation in NaCl.  $v_1$  and  $v_2$  refer to the B1 and B2 phases, respectively. The letters in the calculations column are as in table 1.  $\Delta v = 100(v_1 - v_2)/v_1$ .

	Calc.	Method	Functional	$P_t$	$v_1$	$v_2$	$\Delta v$
LDA	(a)	PS-PW	W	27.0			4.5
	(c)	LAPW	W	21.4			4.7
	(d)	LAPW	HL	21.4			4.7
	(f)	ION	CA	11			
	(g)	ASA+E	HL	26.5	28.5	26.8	6.6
HF and	(i)	LCAO		39.2	28.9	27.7	4.3
	(j)	LCAO	CS75	37.2	27.7	26.4	4.6
HF+corr.	(k)	LCAO	P86	30.1	28.6	27.2	4.8
	(l)	LCAO	P91	28.9	29.0	27.6	4.9
Expt.				30 <sup>r*</sup>			4.7 <sup>u</sup>
				29 <sup>s,t*</sup>			5.8 <sup>r,t</sup>
							5.0 <sup>s</sup>

\* Room-temperature values.  
 (r) From [44]. (t) from [48].  
 (s) from [45]. (u) from [46].

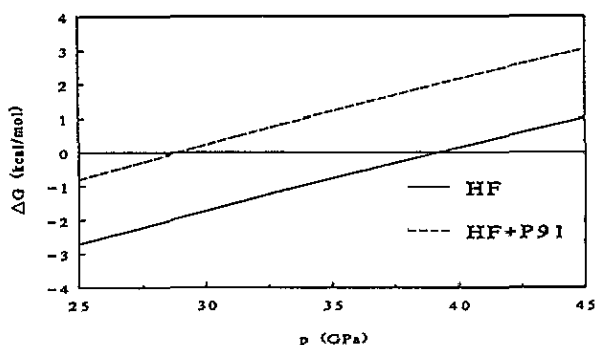
2.2. The B2 (CsCl) phase and the B1–B2 transition

In figure 2 the calculated equations of state for the two phases are reported and compared with the experimental room-temperature data of Sato-Sorensen [47] for the B1 phase and of Heinz and Jeanloz [48] for the B2 phase. Sato-Sorensen also collected data for the B2 phase [47], but, as has been emphasized by many authors [24, 30, 48], these data appear to be affected by systematic errors, and are not reported in figure 2. The theoretical curve refers to HF energies corrected with the correlation contribution evaluated according to P91. The bare HF curve, not shown in the figure, overestimates the B1 and B2 volumes at each pressure, as also indicated by the  $a_c$  value in table 1. The theoretical static-limit data have been corrected for the zero-point and temperature effects according to the prescription of Feldman and co-workers [26]: for the B1 phase  $p(\text{room temp.}) - p(\text{static}) = 1 \text{ GPa}$  (volume independent); for the B2 phase  $p(\text{room temp.}) - p(\text{static}) = 1.4 \text{ GPa}$  (essentially volume independent in the range of pressure here considered (see also [49])). The figure shows the quite good agreement between the present and the Sato-Sorensen data for B1, the difference being always smaller than the experimental error bar. The calculated volume  $V$  at a given pressure is always smaller than the experimental one ( $V/V_{\text{exp}} = 0.98$  at  $p = 0$ ). A similar trend is shown by the Froyen and Cohen [24] and Bukowinski and Aidun [30] data at high pressure. For the B2 phase the situation is similar: agreement between calculated and experimental data

is, in general, good: the  $(V/V_{\text{exp}})$  ratio at  $p = 0$  is 0.93; at  $p \neq 0$  our calculated volumes are smaller than the experimental ones; the same trend is shown by the curves of Feldman and co-workers (figure 1 of [26]). Table 2 summarizes the experimental and the theoretical data for the B1–B2 transition. From the data reported above for zero-point and temperature effects on the  $p$  against  $V$  curve, it turns out that the transition pressure is essentially the same at room temperature and at the static limit. In figure 3 the calculated free energy for the two phases is reported, as a function of the pressure.

**Table 3.** Lattice energy (LE in kcal mol<sup>-1</sup>), lattice constant ( $a_0$  in Å) and bulk modulus ( $B$  in GPa) for the B2 phase of NaCl, from Hartree–Fock-based calculations. The meaning of the acronyms (in the method column) is given in the text. The letters in the calculations column are as in table 1.

Calc.	Method	LE	$a_0$	$B$
(i)	HF	168.7	3.57	24.4
(j)	HF+CS75	183.7	3.41	35.5
(k)	HF+P86	182.5	3.39	35.6
(l)	HF+P91	186.7	3.41	33.8



**Figure 3.** Calculated free energy difference (B1–B2) as a function of pressure.

At the HF level,  $P_t$  (the transition pressure) is overestimated by about 30%. The correction with the CS75 functional slightly changes this number, whereas the P86 and P91 functionals greatly improve the calculated  $P_t$ . It may be noted that, even for this quantity, as for LE,  $a_0$  and  $B$ , the most recent functional performs better than the previous ones. As regards the transition volume differences, the correlated data are in better agreement with experiment than the HF data, and about 15% smaller than the experimental value.

As regards previous calculations, the transition pressure obtained by Froyen and Cohen [24] and by Rodriguez and Methfessel [29] are quite close to the experimental data. However, Feldman and co-workers (calculation (c)) using the same functionals and a fairly complete basis set, found a much lower  $P_t$  value. The transition volume obtained in calculation (a), (c) and (d) with both functionals (HL and W) are in good agreement with the experimental data.

One of the points discussed by Heinz and Jeanloz [48] is the relative magnitude of the bulk modulus of the two phases. From their experimental data these authors conclude that “the bulk modulus decreases by about 6% at the transition from the B1 to the B2 phase ... this result qualitatively confirms the prediction, based on a lattice model, that the bulk modulus would decrease by about 8 to 12% at the B1–B2 transition of NaCl”. As shown by the data of tables 1 and 2, the B2 bulk modulus at zero pressure resulting from the present calculation is *larger* (by about 7%) than that of the B1 phase both at the HF and HF plus

correlation level. Similar results have been obtained by Feldman and co-workers [26] and Bukowski and Aidun [30]. Figure 4 shows that the bulk modulus of the B2 phase remains greater than that of the B1 phase even at high pressure, in agreement with the findings of [26].

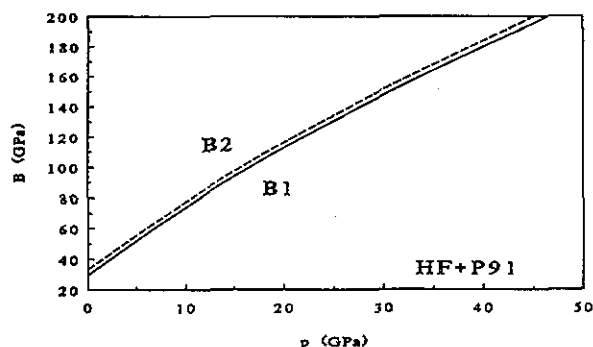


Figure 4. Theoretical results for the pressure dependence of the bulk modulus for NaCl in the B1 and B2 phases.

### 3. Conclusions

The Hartree–Fock LCAO scheme when applied to the study of the equations of state of NaCl produces relatively large errors (+4% for  $a_0$ , –20% for  $B$  and +30% for the B1–B2 transition pressure), which are due to correlation effects (both interionic and intraionic) disregarded at the Hartree–Fock level. The error is larger than in other compounds where covalent bonds are involved (the mean lattice parameter error is +1.2% for 17 semiconductors [22]; less than 1% for silicates [50, 51]), or where the electrostatic contribution is larger, as for example in II–VII [52], I–VI [6] or II–VI [7] compounds.

A simple model for taking into account the correlation effects through the *a posteriori* correction of the HF energy has been checked with encouraging results. It turns out that the most modern and parameter-free functional, P91, produces systematically better results than previous proposals (CS75, P86, Becke [39] and *non-gradient-corrected* correlation functionals). On the whole, the HF+P86 or HF+P91 results are of the same quality as the most reliable LDA results.

If the trends shown in tables 1 and 2 are confirmed by further studies, it appears that the correlation energy can be accurately estimated using modern functionals. Alkali halides, because of their simplicity (two atoms per cell, and high symmetry) are ideal benchmarks for testing computational schemes and for understanding the relative importance of the different forces involved (Coulomb, exchange, short-range correlation, dispersion). Work is in progress [53] for an extension of the present scheme to other members of the same family.

### Acknowledgments

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