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Ab initio Hartree–Fock treatment of ionic and semi-ionic compounds: state of the art

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The periodic *ab initio* Hartree–Fock approach is applied to the Li, Na, K, Be, Mg, Ca and Mn oxides, and to Al_2O_3 (corundum) and SiO_2 (α-quartz). A local basis set ('atomic orbitals') is used. The equilibrium geometry, the formation energy and the bulk modulus are calculated, with reasonable agreement with experiment. The influence of the environment on the oxygen ions is discussed through the Mulliken population and band structure data.

1. Introduction

The static and dynamic properties of ionic and semi-ionic crystals have usually been calculated by semi-classical methods based on Born-type semi-empirical formulae for the interatomic potential energy. An overview of the theory and of the different fields of application can be found in Catlow & Mackrodt (1982). The simplicity of the algorithm allows the investigation of complicated structures, including bulk defects and surface phenomena. On the other hand the nature of the method requires a careful analysis of the results when applied in conditions different from those in which the parameters have been determined. Obviously, no information concerning the wavefunction can be obtained from semi-classical techniques.

Recent advances in the speed and accuracy of the *ab initio* ('first principle') methods now permit the calculation of many ground state properties of simple ionic compounds. The *ab initio* methods can be considered at present as complementary tools to the semi-classical techniques, to which they can provide input data for the parameterization as an alternative to the experiment.

In this paper we present results obtained with our periodic *ab initio* Hartree–Fock CO (crystalline orbitals), LCAO (linear combination of atomic orbitals) program CRYSTAL (Pisani *et al.* 1988; Dovesi *et al.* 1992). In the past five years CRYSTAL has been applied to many ionic systems as well as to semiconductors (Causà *et al.* 1991), and molecular crystals (Dovesi *et al.* 1990) by different authors and at different levels of sophistication (basis set; numerical tolerances adopted in the calculation; use of all-electron or pseudopotential approaches). On the whole the agreement with experiment, when available, is satisfactory; on the other hand, to assess the quality of the results produced by a given method, it is important to refer to a relatively wide class of systems (and properties) investigated with basis sets of equivalent quality and at a comparable level of numerical accuracy. In this paper we perform such an analysis on a set of oxides: fully ionic (Li_2O, Na_2O, K_2O; BeO, MgO, CaO) as well as semi-ionic (corundum and α-quartz) systems will be considered; preliminary results

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Table 1. *Basis sets used in the present study*

(The 'atomic orbitals' (AOs) are contractions of n gaussian type functions (GTFs); a GTF is the product of a gaussian times a polynomial in x, y, z. The AOs sharing the exponents of the GTFs are grouped in shells (s, sp and d shells). In the table the first contraction refers to an s shell, the others to sp shells. So, for example, 6-1 in the lithium case means that the basis consists of 5 AOs resulting from one s shell (contraction of six GTFs) and one (single gaussian) sp shell. The star means that d orbitals are included; in Mn two sets of d functions are used (4-1 contraction); in Ca and K contraction of three GTFs is used, while for Si, Al and O a single gaussian d shell is adopted. In the MnO case, small core (SC) pseudopotentials (PS) are used for Mn (Hay & Wadt 1985) and O (Durand & Barthelat 1975); in this case the first shell is sp. The exponents of the most diffuse gaussians are reported. In all cases the basis set has been optimized in the bulk.)

	cation				anion			
system		α^{sp}_{n-1}	α^{sp}_{n}	α^{d}		α^{sp}_{n-1}	α^{sp}_{n}	α^{d}
Li_2O	6-1	—	0.53	—	8-4-1-1	0.45	0.15	—
Na_2O	8-5-1-1	0.55	0.27	—	8-4-1-1	0.46	0.14	—
K_2O	8-6-5-1-1*	0.39	0.22	0.39	8-4-1-1	0.47	0.13	—
BeO	5-1-1	2.34	0.66	—	8-4-1-1	0.54	0.23	—
MgO	8-5-1-1	0.68	0.28	—	8-4-1-1	0.50	0.19	—
CaO	8-6-5-1-1*	0.45	0.25	0.38	8-4-1-1	0.50	0.17	—
Al_2O_3 (corundum)	6-2-1*	—	0.16	0.43	6-2-1*	—	0.35	0.8
SiO_2 (α-quartz)	6-2-1*	—	0.13	0.50	6-2-1*	—	0.36	0.8
MnO	PS–SC 3-1-1-1*	0.50	0.20	0.22	PS 4-1	—	0.22	—

for MnO will also be presented. Previous HF results on the above systems can be found in Dovesi *et al.* (1991), Lichanot *et al.* (1992), Causà *et al.* (1986), Silvi *et al.* (1992), Salasco *et al.* (1991) and Dovesi *et al.* (1987); references for the experimental data quoted in the following tables can be found in those papers, if not otherwise stated. The formation energy, equilibrium geometry, bulk modulus and elastic constants have been investigated; Mulliken population and band structure data will be used for characterizing the nature of the chemical bonds.

All but the MnO data can be reproduced with the version of the code distributed by the authors (Dovesi *et al.* 1992). It must be stressed that the HF–CO–LCAO method, as implemented in CRYSTAL, can be applied both to surface problems and to the study of neutral local defects with a supercell approach, with an accuracy similar to that documented below for the bulk properties. For reasons of space we will not report data referring to those applications.

2. The method and the basis set

We refer to previous papers for a discussion of the HF–CO–LCAO method. The scheme is affected by three different sources of error.

1. Numerical errors associated with the approximate treatment of the infinite Coulomb and exchange series and the reciprocal cell integration; numerical errors in the fitting procedure for obtaining the first and second derivatives of the energy. It can be shown that for the present compounds such errors are quite small (less than 2% for the elastic constants, which are second derivatives of the energy; negligible for the other properties).

Table 2. *Calculated and experimental equilibrium geometry and bulk modulus*

(a and c are the lattice parameters of unit cell and are given in ångstroms; x, y, z are fractionary coordinates of the indicated atom; the bulk modulus is in GPa; the underlined data have been extrapolated to the static limit, the others refer to room temperature. For the experimental sources, see text.)

		geometry parameters			bulk modulus	
system	space group	param.	calc.	exp.	calc.	exp.
Li_2O	Fm3m	a	4.57	$\underline{4.57}$	93	$\underline{89}$
Na_2O	Fm3m	a	5.48	5.55	58	—
K_2O	Fm3m	a	6.47	6.44	35	—
BeO	$P6_3mc$	a	2.68	2.68	253	214, 220
		c	4.34	4.35	—	224, 245
		x_O	0.380	0.377	—	—
MgO	Fm3m	a	4.20	$\underline{4.19}$	186	$\underline{167}$
CaO	Fm3m	a	4.87	$\underline{4.79}$	128	$\underline{120}$
Al_2O_3 (corundum)	$R\bar{3}c$	a	4.74	4.76	—	—
		c	13.03	12.99	—	—
		z_{Al}	0.354	0.352	—	—
		z_O	0.304	0.306	—	—
		V	253.29	254.98	—	—
SiO_2 (α-quartz)	$P3_221$	a	4.93	4.92	—	34–37
		c	5.42	5.40	—	—
		z_{Si}	0.470	0.470	—	—
		x_O	0.412	0.414	—	—
		y_O	0.269	0.267	—	—
		z_O	0.117	0.119	—	—
		V	114.13	113.12	—	—
MnO	Fm3m	a	4.53	$\underline{4.44}$	152	147

2. Basis set limitations. The adopted basis set, as summarized in table 1, is probably close to a triple zeta basis set in a molecular context; as will be shown with reference to the properties of MgO (table 4), it can be assumed that the error associated with the use of the present basis sets is quite small for many of the properties investigated here.

3. The correlation error. It is well known that the Hartree–Fock method disregards the instantaneous interelectronic interactions. The largest part of the difference between the calculated and experimental data to be discussed below is to be attributed to such an approximation. Methods exist for overcoming the limitations of the HF approach, which are common practice in molecular quantum chemistry (Wilson 1984). No standard implementation of these techniques for periodic systems exists at present. A simple correction of the HF total energy is possible, however, through correlation only density-functional schemes (Colle & Salvetti 1975; Perdew 1986, 1991), that have been shown to perform quite well for semiconductors (Causà *et al.* 1991); such a correction has been applied in the present paper in the evaluation of the HF formation energy.

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Table 3. *Experimental and calculated binding energies* (hartree)

(The correlation corrections are evaluated according to the Colle & Salvetti (1975 (CS)) and Perdew's (1986 (P86) and 1991 (P91)) functionals. The numbers in parenthesis are the percentage errors with respect to the experiment.)

system	HF	HF+CS	HF+P86	HF+P91	exp.
Li_2O	0.300	0.403	0.410	0.399	0.439
	(−32)	(−8)	(−7)	(−9)	
Na_2O	0.189	0.277	0.286	0.276	0.331
	(−44)	(−16)	(−14)	(−17)	
K_2O	0.138	0.224	0.249	0.234	0.293
	(−54)	(−24)	(−15)	(−20)	
BeO	0.339	0.416	0.432	0.426	0.446
	(−24)	(−7)	(−3)	(−4)	
MgO	0.269	0.342	0.361	0.356	0.377
	(−29)	(−9)	(−4)	(−6)	
CaO	0.279	0.357	0.376	0.371	0.399
	(−30)	(−10)	(−6)	(−7)	
Al_2O_3	0.894	1.124	1.174	1.159	1.161
	(−23)	(−3)	(+1)	(0)	
SiO_2	0.512	0.649	0.675	0.667	0.704
	(−27)	(−8)	(−4)	(−5)	
MnO	0.232	0.318	0.344	0.338	0.343
	(−32)	(−7)	(0)	(−1)	

3. Results and discussion

In table 2 the geometry optimized with the basis sets of table 1 are reported and compared with the experimental data; where possible, the latter have been corrected for the zero point and temperature effects (static limit). It turns out that the error is negligible for Li_2O, BeO, MgO; below 1% for SiO_2, Al_2O_3 and Na_2O (although we note that we were not able to find thermal expansion data for the latter system and for K_2O, for which the temperature effects are expected to be quite large; using the thermal expansion data of NaF and KF, an athermal limit of 5.49 Å† and 6.38 Å is obtained for the two systems); between 1 and 2% for CaO and K_2O; in the case of MnO the error is about 2%. The error increases along the series Li, Na, K and Be, Mg, Ca, because of the increasing relative importance of dispersion and intraionic correlation effects with respect to the Coulomb and short-range repulsion terms. In extreme situations, where large cations are involved, as for example with rubidium or silver halides, the error can be as large as 10% (Aprà *et al.* 1991). The last two columns of table 2 report the calculated and experimental bulk moduli. The HF results are always larger by about 10% than the experimental data, in line with molecular experience (Hehre *et al.* 1986).

In table 3 the binding energy (BE) evaluated with respect to the isolated atoms is reported. The HF BE is 20 to 50% smaller than the experimental one, due to the large correlation contribution to the bond formation. The third, fourth and fifth columns show the binding energy obtained after adding *a posteriori* correlation contributions to the HF energy, by integrating the HF charge density with the formulae proposed by Colle & Salvetti (1975) and Perdew (1986, 1991). The three functionals appear to perform roughly equivalently; the HF error is always reduced; the final BE remain,

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† 1 Å = 10^{-10} m = 10^{-1} nm.

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Table 4. *Basis set effects on bulk properties of* MgO *in the rocksalt structure*

(Basis set (c) is described in table 1. (d) and (e) are obtained by adding a single gaussian d-shell to oxygen and magnesium respectively ($\alpha = 0.65$ bohr^{-2} in both cases). (b) is obtained from (c) by contracting one more gaussian into the valence inner shell of magnesium and reoptimizing the outer gaussian shell ($\alpha = 0.40$ bohr^{-2}); (a) is obtained from (b) performing a similar contraction on oxygen ($\alpha = 0.21$ bohr^{-2}). t_1 and t_2 are the CPU times (in CRAY-YMP seconds) required by the integral and SCF part for the calculation of a single energy point. E_{tot} and BE (in hartrees) are the total and binding energies; a_0 (in ångströms) is the lattice parameter; B, C_{11}, C_{12} and C_{44} (in GPa) are the bulk modulus and the elastic constants. The number of atomic orbitals per unit cell is 18, 22, 26, 31 and 36 from (a) to (e). The experimental data at the athermal limit are 314, 94, 160 GPa for C_{11}, C_{12} and C_{44} respectively (Sumino *et al.* 1983).)

	basis set										
	cation	anion	t_1	t_2	E_{tot}	BE	a_0	B	C_{11}	C_{12}	C_{44}
(a)	8-61	8-51	32	2	−274.6724	0.267	4.193	195	384	100	199
(b)	8-61	8-411	39	4	−274.6741	0.268	4.201	186	357	100	190
(c)	8-511	8-411	67	5	−274.6748	0.269	4.205	181	340	101	185
(d)	8-511	8-411*	98	7	−274.6752	0.270	4.205	182	333	105	184
(e)	8-511*	8-411*	144	9	−274.6799	0.274	4.195	183	326	111	183

however, in all cases smaller than the experimental result (Lide 1991) by something between 0 and 20%. A comparison with the results of a similar study on semiconductors (seventeen III–V systems (Causà *et al.* 1991)) seems to indicate that for ionic compounds the *a posteriori* DF correction is less effective than for covalent systems: in the former case the error (after the P86 correction) was nearly independent of atomic number, and the mean error was 2.5%, whereas in the present case it is greater than 4%.

In table 4 the effect of the basis set on the static properties of MgO is documented. Basis set (a) is relatively poor, although more flexible than a minimal basis set. At the other extreme, basis set (e) is quite complete, containing three valence sp shells on oxygen and two valence sp shells on magnesium; a set of polarization functions is included on both atoms. If we take as a reference basis set (a), the table shows that it is important to provide oxygen additional variational freedom for allocating the two extra electrons coming from magnesium; from (b) on, however, the properties remain essentially constant as the basis set is enlarged. The exceptions are the C_{11} and C_{12} elastic constants; the important role of d functions, documented in the table, is related to the polarization of both the cation and of the anion, allowed by the reduced symmetry of the atomic site in the deformed unit cell. We note that the large Cauchy violation exhibited by MgO is well reproduced by the HF theory.

Figure 1 offers another example of application of the HF–LCAO technique; CaO undergoes a B1 (‘NaCl structure’) to B2 (‘CsCl structure’) phase transition at about 60–70 GPa (Mammone *et al.* 1981). Theoretically, such a transition has been studied, among others, by Mehl & Cohen (1988) with an LAPW technique (transition pressure 54 GPa); previous calculations with the CRYSTAL program performed by using pseudopotentials (D'Arco *et al.* 1992; 68 GPa) or smaller basis sets (D. M. Sherman, personal communication; 74 GPa) produced a transition pressure quite close to the present one (70 GPa) and in reasonable agreement with experiment.

In table 5 the Mulliken population data for the systems investigated are reported. The oxygen net charge is very close to $-2\,|e|$ for the Li, Na, K and Mg compounds; around $-1.8\,|e|$ for CaO and BeO and $-1.5\,|e|$ for MnO. It is $-1.2\,|e|$ and $-1.0\,|e|$ in

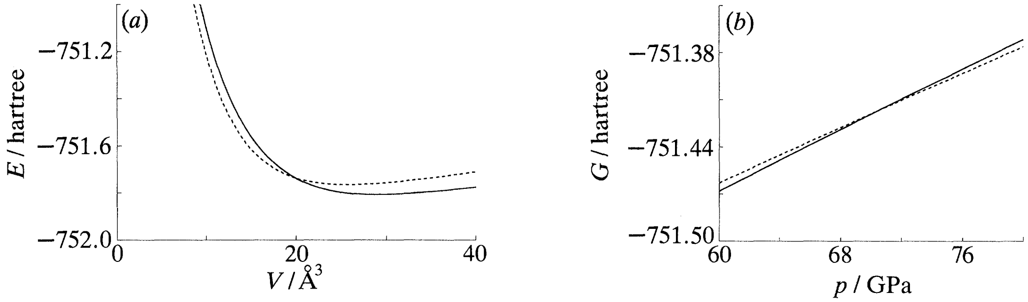

Figure 1. (*a*) Total energy of CaO in the B1 and B2 phases as a function of the unit cell volume. (*b*) Calculated free energy against pressure curves for CaO in the B1 and B2 phases. ———, B1; - - - - -, B2.

Table 5. *Mulliken population analysis data*

(q(O) is the oxygen net charge; B(i–j) is the bond population; $r_{\mathrm{O}}(r_{\mathrm{X}})$ is the square root of the anion (cation) spherical second-order moment; the electronic charge density is partitioned according to a Mulliken analysis. N is the coordination number of the oxygen atom; R(X–O) and R(O–O) are the shortest distances between the indicated atoms. Distances in bohrs.)

system	q(O)	q(X)	B(X–O)	B(O–O)	r_{O}	r_{X}	N	R(X–O)	R(O–O)
Li_2O	−1.937	0.969	−0.007	−0.020	4.42	0.98	8	3.74	6.11
Na_2O	−2.067	1.034	−0.028	−0.003	4.83	2.45	8	4.54	7.42
K_2O	−2.014	1.007	−0.050	−0.001	4.79	4.33	8	5.27	8.60
BeO	−1.746	1.746	0.043	−0.017	4.07	1.07	4	3.09	5.04
MgO B1	−1.947	1.947	−0.004	−0.025	4.32	2.24	6	3.97	5.61
MgO B2	−1.824	1.824	0.012	−0.096	4.22	2.42	8	4.34	5.01
CaO B1	−1.833	1.833	−0.018	−0.001	4.40	4.00	6	4.60	6.50
CaO B2	−1.877	1.877	−0.020	−0.051	4.33	3.95	8	4.83	5.57
Al_2O_3	−1.220	1.830	0.148	−0.020	3.84	3.18	3	3.50	4.77
			0.107				3	3.72	
SiO_2	−1.018	2.036	0.290	−0.010	3.73	3.76	4	3.04	4.94
MnO	−1.465	1.465	0.034	−0.008	4.16	4.45	6	4.31	6.10

corundum and α-quartz respectively. In the BeO case the 0.2 electron difference with respect to fully ionic bonding is due to the important participation of the p orbitals of the cation; a similar role is played by the d orbitals of Ca in CaO (0.18 electrons). The B(X–O) column provides information for the characterization of the bonds; negative values indicate that the interaction between the electrons of the cation and the anion is repulsive (short-range repulsive or 'exclusion' forces), as expected for a fully ionic compound; it is to be noted that also from this point of view BeO is 'anomalous' with respect to the other simple oxides (a small positive bond population). The large positive values for corundum and α-quartz are a measure of the covalent character of the X–O bond. According to the B(X–O) values α-quartz is much more covalent than corundum, as expected. Further information can be obtained by B(O–O), which is a measure of the repulsion between the oxygens; in the alkali series, for example, it is much larger in Li_2O than in Na_2O and K_2O, indicating that the equilibrium configuration in the former case is mainly determined by the oxygen–oxygen repulsion; a similar trend is shown by the Be, Mg and Ca series. The comparison of the B2 data for MgO (referring to the equilibrium volume of the B1 phase) and CaO (referring to the equilibrium volume of the B2 phase) shows that the energetics of this

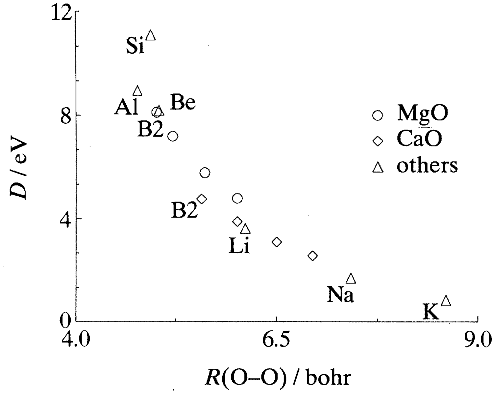

Figure 2. Correlation between the width of the p band of oxygens (eV) and the distance R_{O-O}(Å) between the nearest neighbours oxygen atoms. The three values for MgO refer to $a_0 = 3.90$, 4.20 (equilibrium) and 4.50 Å; for CaO to 4.20, 4.87 (equilibrium) and 5.20 Å. Two points (one for MgO and one for CaO) referring to the B2 (CsCl) structure are also reported. For the other oxides only the cation is indicated.

more closely packed structure are essentially determined by the O–O repulsion. The r_O and r_X columns compare the calculated radii of the ions (square root of the spherical second-order moment evaluated after partitioning the electronic charge of the unit cell according to Mulliken). It turns out that the size of the oxygen atom is quite different for ionic and covalent compounds; data not reported in the table show that r_O exhibits considerable change when the system is compressed, supporting the need of 'breathing' terms in semi-classical models of the oxides (Schroeder 1966).

The density of states of the ionic compounds is very simple: the bands are flat, separated by large gaps; each band can be characterized in terms of a particular atomic orbital of the atoms of the unit cell; in the case of the oxides, the highest valence bands are always oxygen (non-bonding) p bands; the participation of the cation to those bands is negligible; the 'dispersion' of the band (and thus the bandwidth) is a measure of the interaction between the oxygens. Figure 2 correlates the width of the oxygen p bands with R(O–O), the distance between first neighbours oxygens (the coordination of the oxygen atom is given in table 5). The figure shows that a similar correlation exists for the compounds investigated with the exception only of SiO_2, which appears to belong to a different 'family' due to its strong covalent character.

4. Conclusions

The Hartree–Fock LCAO technique, as implemented in CRYSTAL, has been shown to provide reasonable results and useful interpretation schemes in the study of ionic and semi-ionic compounds. Given its availability from the authors and the relatively low cost of the calculations, CRYSTAL can be considered a standard tool in the study of the electronic structure of simple ionics, and a useful complement to semi-classical methods.

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