

Ab initio pseudopotential description of cohesion in NaCl

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We present the first *ab initio* pseudopotential calculation of the cohesive properties of NaCl. The theoretical results for the equilibrium lattice constant and the bulk modulus are in good agreement with experiment. Our physical picture of cohesion is contrasted to that of widely used models.

The use of the local-density-functional scheme¹ for the description of many-electron interactions in solids has led to considerable progress in the theoretical understanding of structural properties of solids. This was aided by the introduction of first-principles pseudopotentials^{2,3} in the local density scheme. In particular, very accurate results have been obtained for a number of semiconductors⁴ and metals.⁵ In this Communication we extend the *ab initio* pseudopotential scheme to the description of cohesion in insulators with ionic character. We take NaCl as an example.

For the ionic pseudopotentials of Na and Cl, we use the Hamann-Schlüter-Chiang *l*-dependent pseudopotentials,³ whose general analytic form is given by⁶

$$V_l^{(i)}(r) = V_{\text{loc}}^{(i)}(r) + \tilde{V}_l^{(i)}(r), \quad i = \text{Na or Cl},$$

where a local (*l*-independent) potential is defined by

$$V_{\text{loc}}^{(i)}(r) = -\frac{1}{r} \sum_j z_j^{(i)} \text{erf}(-\alpha_j^{(i)} r), \quad (1a)$$

with

$$\sum_j z_j^{(i)} = Z_i,$$

and where nonlocal corrections are given by

$$\tilde{V}_l^{(i)}(r) = \sum_{j=1}^3 (a_{j,l}^{(i)} + b_{j,l}^{(i)} r^2) \exp(-\beta_{j,l}^{(i)} r^2). \quad (1b)$$

The coefficients in Eqs. (1a) and (1b) are given in Table I. For $l \geq 2$, the nonlocal part \tilde{V}_l is assumed to be zero, in agreement with the fact that there are no orthogonality effects.

TABLE I. Ionic pseudopotential parameters [Eqs. (1a) and (1b)] (atomic units).

	\tilde{V}_0			\tilde{V}_1		
	$\beta_{j,0}$	$a_{j,0}$	$b_{j,0}$	$\beta_{j,1}$	$a_{j,1}$	$b_{j,1}$
Na						
$z_1 = 5.431$	0.84	-41 680.723 568 7	1 048.528 777 9	0.50	186.010 204 2	-6.021 927 5
$\alpha_1 = 1.63$	0.91	37 433.757 260 2	2 439.485 851 9	0.61	-42.845 128 2	-29.943 911 5
$z_2 = 1.431$	1.11	4 251.662 063 1	280.636 989 0	0.81	-139.289 976 0	-13.640 522 7
$\alpha_2 = 0.52$						
Cl						
$z_1 = 7.0$	0.81	13.971 687 1	-3.394 049 1	1.15	2.539 987 9	-0.565 447 0
$\alpha_1 = 7.86$	2.22	169.258 738 1	-136.331 792 4	2.56	77.008 839 6	-44.949 404 8
	3.68	-162.086 221 6	-129.890 573 3	3.97	-62.801 902 2	-65.127 766 6

We use plane waves as basis functions and obtain convergence with about 500 plane waves treated exactly and another ~ 500 treated by perturbation theory. From the self-consistent charge density of the valence electrons, we calculate the total energy within the local density scheme, as described in Refs. 7 and 8.

Figure 1(a) shows the charge-density contour map of NaCl displayed in the (100) plane, calculated for a lattice constant $a = 5.63 \text{ \AA}$. It clearly illustrates an essentially spherical charge distribution around the anions, in agreement with the familiar picture of ionic bonding.⁹ In the past this picture was partially contradicted by empirical pseudopotential calculations,¹⁰ which predicted a non-negligible directionality in the chemical bonding. Our *ab initio* calculation clarifies

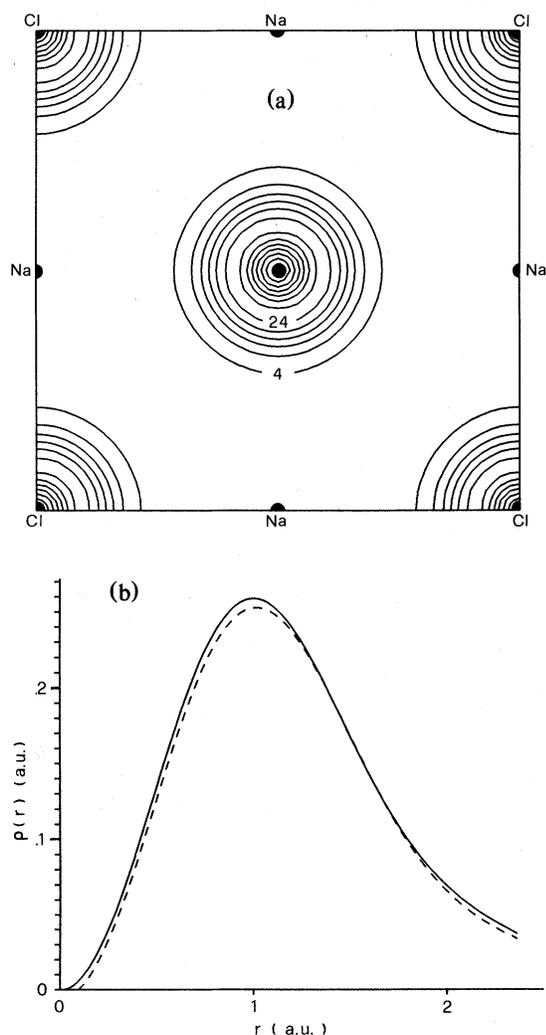


FIG. 1. Charge density of NaCl in units of $1/100 \text{ a.u.}$: (a) in the (100) plane for $a = 5.63 \text{ \AA}$; (b) along the (100) direction for $a = 5 \text{ \AA}$ (solid line) and for $a = 6 \text{ \AA}$ (dashed line).

that this anisotropy was due to the inaccuracy of the empirical pseudopotentials employed.

The overall character of the electronic charge distribution, as given in Fig. 1(a), does not change with the lattice constant. However, as shown in Fig. 1(b), the charge density around the anion is not rigid in detail, but changes with the lattice constant. In particular, we find a non-negligible shrinkage of the electronic charge around the anions, when the interatomic distance becomes smaller. This behavior can be ascribed to either crystal-field or orthogonality effects. We shall discuss this point in a future publication.

Our results confirm the basic picture of the breathing shell model,¹¹ which takes into account the isotropic deformation of the electronic charge distribution either when the ions are brought together to form a crystal or when the crystal is subject to a homogeneous deformation (e.g., due to hydrostatic pressure).

The nonrigid behavior of the charge density determines to a large extent the variation of the total en-

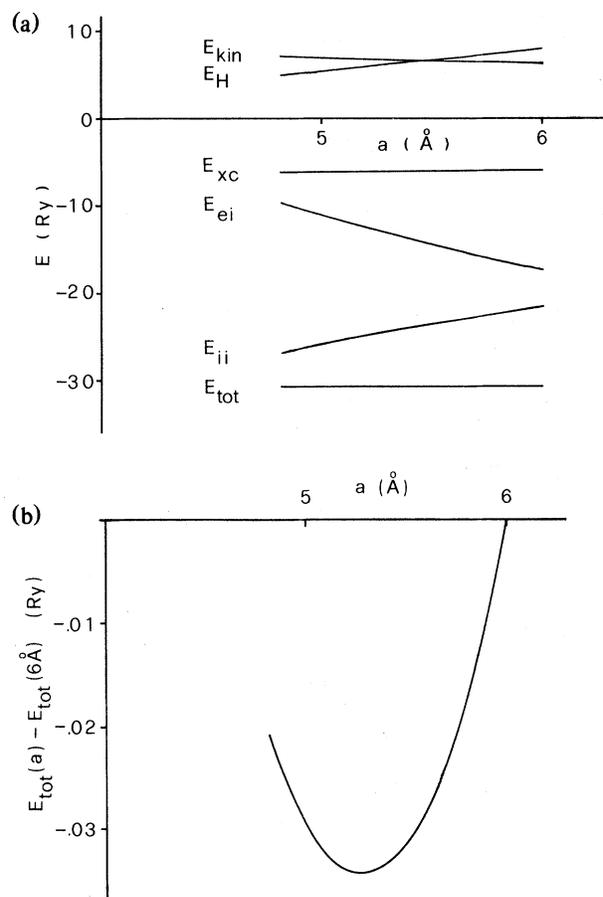


FIG. 2. Results of the total energy calculations (in Ry) as a function of the lattice constant a (in \AA): (a) single contributions (see text); (b) total energy.

ergy terms as a function of the lattice constant. Figure 2(a) shows the variation of the different contributions to the total energy E_{tot} , which we have written as⁸

$$E_{\text{tot}} = E_{\text{kin}} + E_{\text{H}} + E_{\text{xc}} + E_{\text{ei}} + E_{\text{ii}},$$

where E_{kin} , E_{H} , and E_{xc} are the kinetic, Hartree, and exchange-correlation interaction¹² energies of the valence electrons, E_{ei} is the interaction energy of the valence electrons with the free ions, and E_{ii} is the electrostatic ion-ion interaction energy. Each single term depends strongly on the interatomic distance in contrast with the predictions of rigid-ion models.^{13,14} However, when they are summed up, a slowly varying curve is obtained for $E_{\text{tot}}(a)$. Such a weak dependence on the lattice constant corresponds to the high compressibility of NaCl. It implies that an extremely high accuracy is required to obtain the equilibrium lattice constant and the bulk modulus.

We obtain [see Fig. 2(b)] the equilibrium lattice constant of NaCl to within $\sim 6\%$ [$a_{\text{theor}} = 5.28 \text{ \AA}$, while the 0-K value extrapolated from the experimental datum at room temperature is $a_{\text{exp}}(0 \text{ K}) = 5.6 \text{ \AA}$ (Ref. 15)] and the bulk modulus to within 12% [$B_{\text{theor}} = 2.40 \pm 0.3 \times 10^{11} \text{ dyn/cm}^2$ while $B_{\text{expt}} = 2.40 \times 10^{11} \text{ dyn/cm}^2$ (Ref. 16)]. The agreement between theoretical and experimental values is satisfactory in view of the difficulties inherent in any fully *ab initio*

calculation of the equilibrium parameters of a highly compressible material like NaCl. We can thus conclude that an *ab initio* pseudopotential calculation is able to describe cohesion even for highly ionic compounds. The remaining discrepancies can be attributed to both systematic (e.g., exchange-correlation energy) and numerical inaccuracies.

The pseudopotential description differs substantially from the extended rigid-ion approach of Gordon and Kim¹⁴: While we start from the knowledge of the ionic cores, supposed to be frozen, and solve the problem for the valence electrons self-consistently at each lattice constant, Gordon and Kim start from the knowledge of the free ions, supposed to be frozen, and allow the crystal charge to change only because of the mutual overlap of the rigid free ions (Na^+ and Cl^-). Their approach excludes from the beginning the "breathing" of the electronic charge around the anions, which is the key effect in our description of cohesion. Therefore the microscopic picture underlying the Gordon-Kim approach¹⁴ qualitatively differs from the one we obtain from our self-consistent calculation. It will be interesting to confront these two different physical pictures for the case of the pressure-induced phase transition of NaCl from the rocksalt structure to the CsCl structure. This is planned to be the subject of a forthcoming publication.

¹For a review, see M. Schlüter and L. J. Sham, *Phys. Today* **35**, 36 (1982).

²A. Zunger and M. L. Cohen, *Phys. Rev. B* **18**, 5449 (1979).

³D. R. Hamann, M. Schlüter, and C. Chiang, *Phys. Rev. Lett.* **43**, 1494 (1979).

⁴J. Ihm and M. L. Cohen, *Phys. Rev. B* **21**, 1527 (1980); M. T. Yin and M. L. Cohen, *Phys. Rev. Lett.* **45**, 1004 (1980); J. Ihm and J. D. Joannopoulos, *Phys. Rev. B* **24**, 4191 (1981); G. B. Bachelet, H. S. Greenside, G. A. Baraff, and M. Schlüter, *ibid.* **24**, 4745 (1981).

⁵P. K. Lam and M. L. Cohen, *Phys. Rev. B* **24**, 4224 (1981); S. G. Louie, S. Froyen, and M. L. Cohen (unpublished).

⁶G. B. Bachelet, D. R. Hamann, and M. Schlüter (unpublished).

⁷J. Ihm, A. Zunger, and M. L. Cohen, *J. Phys. C* **12**, 4409 (1979).

⁸W. Andreoni and K. Maschke, *Phys. Rev. B* **22**, 4816 (1980).

⁹L. Pauling, *Nature of the Chemical Bond*, 3rd ed. (Cornell University, Ithaca, New York, 1960), p. 506.

¹⁰S. Nagel, K. Maschke, and A. Baldereschi, *Phys. Status*

Solidi (b) **76**, 629 (1976).

¹¹U. Schröder, *Solid State Commun.* **4**, 347 (1966); A. N. Basu, D. Roy, and S. Sengupta, *Phys. Status Solidi* (a) **23**, 11 (1974); A. Ghosh, A. K. Sarkar, and A. N. Basu, *J. Phys. C* **8**, 1332 (1975).

¹²For the exchange-correlation term, we use the Wigner-type interpolation formula as given in Ref. 8.

¹³M. P. Tosi, in *Solid State Physics: Advances in Research and Applications*, edited by F. Seitz and D. Turnbull (Academic, New York, 1964), Vol. 16 p. 1.

¹⁴R. G. Gordon and Y. S. Kim, *J. Chem. Phys.* **56**, 3122 (1972); L. L. Boyer, *Phys. Rev. B* **23**, 3673 (1981), and references therein.

¹⁵The value at room temperature is from R. W. G. Wyckoff, *Crystal Structures* (Interscience, New York, 1960), Vol. 1; the value of the expansion $\Delta a/a$ is from the *American Institute of Physics Handbook*, 3rd ed., edited by D. E. Gray (McGraw-Hill, New York, 1972), pp. 4-139.

¹⁶S. Haussühl, *Z. Phys.* **159**, 223 (1960); see also Ref. 13, p. 44.