

Total energy calculation of perovskite, BaTiO₃, by self-consistent tight binding method

B T CONG*, P N A HUY, P K SCHELLING[†] and J W HALLEY[#]

Faculty of Physics, Hanoi University of Science, 334 Nguyen Trai Street, Hanoi, Vietnam

[†]Argonne National Laboratory, USA

[#]School for Physics and Astronomy, University of Minnesota, USA

Abstract. We present results of numerical computation on some characteristics of BaTiO₃ such as total energy, lattice constant, density of states, band structure etc using self-consistent tight binding method. Besides strong Ti–O bond between 3d on titanium and 2p orbital on oxygen states, we also include weak hybridization between the Ba 6s and O 2p states. The results are compared with those of other more sophisticated methods.

Keywords. Tight binding; perovskite; BaTiO₃.

1. Introduction

Ferroelectric (FE) materials are of importance for a variety of present and potential applications. These include piezoelectric transducers and actuators, non-volatile ferroelectric memories, dielectrics for microelectronics, wireless communications, pyroelectric arrays, and non-linear optical applications (Xu 1991).

The most important class of FE materials is the perovskite oxides, ABO₃. At high temperature they all share the paraelectric simple-cubic perovskite structure with metal *A* at the cube corners, metal *B* at the cube centre and O atoms at the cube faces. As the temperature is reduced, a structural phase transition into a FE state takes place, in which the *B* atom (usually a transition-metal atom) displaces off-centre with respect to the surrounding oxygen octahedron, so that the material develops a spontaneous electric polarization, *P*. In typical FE material, BaTiO₃, the phase transition from high temperature cubic structure to tetragonal one occurs at 393 K. The system becomes orthorhombic at 278 K and rhombohedral below 183 K. In spite of the fact that the perovskites have been the subject of intense investigation since the discovery of ferroelectricity in barium titanate in the 1940s, there is still no complete understanding of the nature of properties of these materials. Several methods were applied for calculation of BaTiO₃. Among them are the first-principle calculations based on the local density approximation (LDA, see for example, Cohen and Krakauer (1990), King-Smith and Vanderbilt (1994)), atomistic modeling (Tinte *et al* 1999) etc. Another efficient method developed for study of oxide compounds is the self-consistent tight binding (SCTB). This method is successfully used for studying two component oxides

such as TiO₂ (Schelling *et al* 1998) and MnO₂ (Zhuang and Halley 2001). In this work, we apply the SCTB for calculation of three-component perovskite system, BaTiO₃.

The starting point of SCTB method (Schelling *et al* 1998) is very close to the density functional method formulated by Hohenberg and Kohn (1964) where the ground state of many body electron system is found using the variational principle of total energy functional with respect to electron degree of freedom. The expectation value of the total energy is written as

$$E_{\text{tot}} = T + V_1 + V_2 + V_3,$$

where *T*, *V*₁, *V*₂, *V*₃ correspond to the kinetic energy, one electron potential energy, electron–electron interaction and ion–ion Coulomb energy. Two first terms (third) may be written by using one-body (two-body) density matrix, $\mathbf{r}_1(\vec{r}, \vec{r}')$, ($\mathbf{r}_2(\vec{r}, \vec{r}'; \vec{r}, \vec{r}')$). Single-particle wave function, $\mathbf{y}_1(\vec{r})$, is eigenfunction of one-body density matrix and satisfied the following integral equation

$$\int d\vec{r}' \mathbf{r}_1(\vec{r}, \vec{r}') \mathbf{y}_1(\vec{r}') = n_1 \mathbf{y}_1(\vec{r}),$$

*n*₁ is equal to either 1 or 0 as in Hartree–Fock and LDA theory. It is also interpreted as occupation numbers of one-electron orbital. $\mathbf{y}_1(\vec{r})$ can be expanded in the series of tight binding orthogonal orbital, \mathbf{f}_{in} localized at site *i*, $\mathbf{f}_{in}(\vec{r})$ as

$$\mathbf{y}_1(\vec{r}) = \sum_{in} c_{in,1} \mathbf{f}_{in}(\vec{r}).$$

In terms of such basis, the total energy functional with constraint

$$\sum_{im} c_{im}^* c_{im} = 1,$$

*Author for correspondence

is written as

$$\begin{aligned}
E_{\text{tot}} &= \sum_i E_i(\{Q_i\}) \\
&+ \sum_{im,jn} Q_{im,jn} [(1-d_{ij})t_{im,jn} + v_{im,jn}^1] \\
&+ \frac{1}{2} e^2 \sum_{i,j} \frac{(Z_i - Q_i)(Z_j - Q_j)}{R_{ij}} \\
&- \sum_I n_I \mathbf{e}_I \left(\sum_{im} c_{im,I}^* c_{im,I} - 1 \right), \\
Q_{im,jn} &= \sum_I n_I c_{im,I}^* c_{jn,I}, \\
v_{im,jn} &= \int d\vec{r} \mathbf{f}_{im}^*(\vec{r}) v^1(\vec{r}) \mathbf{f}_{jn}(\vec{r}), \\
t_{im,jn} &= \int d\vec{r} \mathbf{f}_{im}^*(\vec{r}) \left(\frac{-\mathbf{H}^2 \nabla^2}{2m} \right) \mathbf{f}_{jn}(\vec{r}).
\end{aligned} \tag{1}$$

The sum, $Q_i = \sum_n Q_{i,n}$, can be interpreted as the number of electrons at site i . Here we assume that onsite terms contribute an energy of the form $\sum_i E_i(\{Q_i\})$. The term, $E_i(\{Q_i\})$, is onsite electron energy depending on the number of the electron on the site and also on the locations of neighbouring ions. In order to find the ground state, we solve the variation problem, minimizing E_{tot} with respect to the coefficients, $c_{im,I}^*$. The final equation is

$$\begin{aligned}
&\left\{ \frac{\partial E_i}{\partial Q_i} - e^2 \sum_j \frac{(Z_j - Q_j)}{R_{ij}} \right\} c_{im,I} \\
&+ \sum_{im,jn} \{ (1-d_{ij})t_{im,jn} + v_{im,jn}^1 \} c_{jn,I} = \mathbf{e}_I c_{im,I},
\end{aligned} \tag{2}$$

where \mathbf{e}_I is the single-particle energy. This is the single-particle equation which is solved by self-consistent procedure: solving (2) with a starting set of charges Q_i to get $\mathbf{e}_I, c_{jn,I}$; to evaluate new charges, $Q_i = \sum_{ml} n_I c_{im,I}^* c_{im,I}$ and to solve (2) with new charges again. This process is iterated until full self consistency is achieved.

2. Application for BaTiO₃

The self-consistent calculations for bulk BaTiO₃ were done with a supercell consisting of $2 \times 2 \times 3$ unit cells with periodic boundary conditions applied in all three dimensions. In the calculation, we include the minimum number consisting of 10 orbitals in basis set: Ba 6s, Ti 3d, and O 2s, 2p. The onsite energy, $E_i(\{Q_i\})$, is written

as sum of the intrasite energy, E_i^∞ , and environmental term, E_i^{env} , $E_i = E_i^\infty + E_i^{\text{env}}$

$$E_i^\infty = \sum_1 A_1 Q_i^1;$$

$$E_i^{\text{env}} = \sum_{i=0, j \in (\text{Ba, Ti})} Q_i \sum_n a_n \left[\frac{R_{ij}^0}{R_{ij}} \right]^n + \sum_s \mathbf{e}_s Q_{is},$$

where s means shell and $Q_{i,s}$ is the number of electrons in shell s of ion i . The shells correspond to the orbital basis chosen for the tight binding model and are s, p for oxygen, s for Ba, d for Ti. \mathbf{e}_s is energy of the one-electron Hartree–Fock orbital of the neutral atom in shell, s . R_{ij}^0 is equilibrium bond length and R_{ij} is bond length. Here, E_i^∞ is parametrized using polynomial form of charge Q_i . Coefficients A_1 in E_i^∞ are determined from fitting to the experimental ionization energies and electron affinities for Ba, Ti and O. Results for E_i^∞ when its neighbours are far away for the ions of interest are shown in figure 1.

The first sum in environmental dependent part, E_i^{env} , is evaluated only for nearest neighbour titanium–oxygen and barium–oxygen pairs and because of this term, we need not add any purely classical interatomic potentials. The environmental term effectively produces a repulsive interaction between titanium–oxygen and barium–oxygen pairs which act to stabilize the crystal. The a_n coefficients are determined by fitting with the total energy given by the first-principle calculation of fourth order in soft-mode displacement theory (King–Smith and Vanderbilt 1994). The constants were chosen for the case without strain (in atomic unit) as $\mathbf{k} = -0.0175$, $\mathbf{a} = 0.32$, $\mathbf{g} = -0.473$. The value of a_n for pairs of sites are given in table 1.

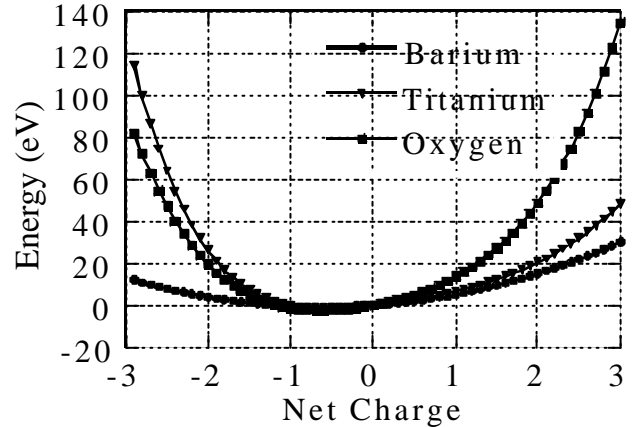


Figure 1. The functions, $E_i^\infty(Q_i)$ describing the intrasite energy.

Table 1. Coefficient, a_n , in the parametrization form for E_i^{env} .

	a_1	a_2	a_3	a_4	a_5
Ba_O	0.1	0.2	0.02	0.006	0
Ti_O	0.06	0.36	0.01	0.05	0.01

With these values of a_n parameters, one can compute the value of the lattice constant which minimizes the cohesive energy (figure 2).

The minimum of energy gives the equilibrium lattice constant for BaTiO₃ in cubic phase as $a_0 = 3.992 \text{ \AA}$. This value agrees well with the experimental lattice constant in the cubic phase, $a = 3.995 \text{ \AA}$ obtained by extrapolation to 0 K (Kay and Vousden 1949).

Figure 3 shows energy as function of $a - a_0$ (in a.u.) for a comparison with LDA and shell model (Tinte *et al* 1999), a_0 is the equilibrium lattice parameter. In the SCTB calculation for the bulk BaTiO₃, the charges on the different kind of sites are found and tabulated in table 2 (for comparison with other methods, the results of different calculations are also listed).

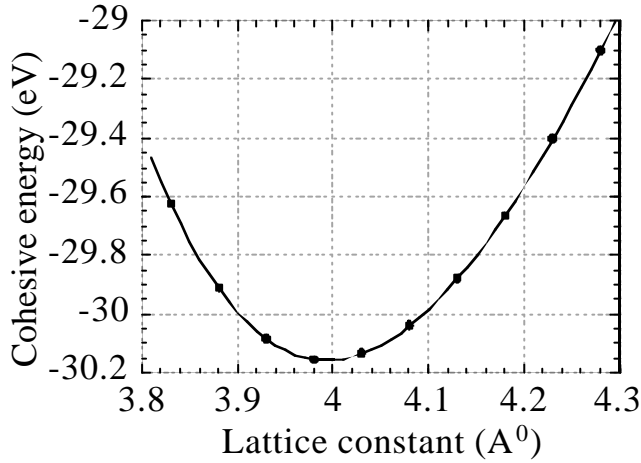


Figure 2. Cohesive energy for BaTiO₃ as a function of lattice constant.

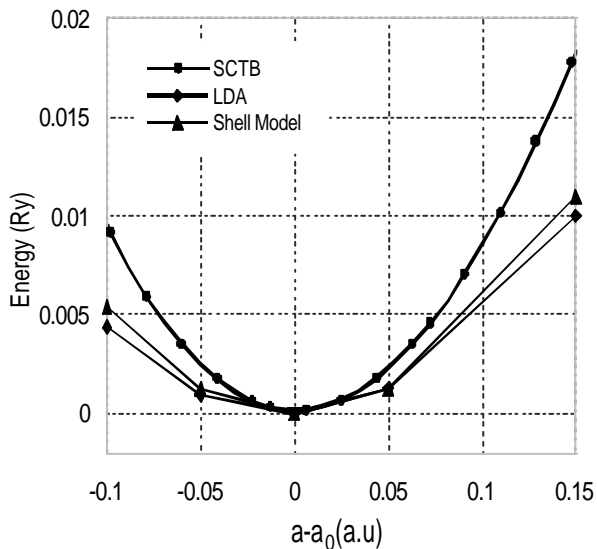


Figure 3. The same curve as in figure 2 but plotted in a.u. and compared with LDA, shell model.

Figure 4 shows the dependence of energy on several structural distortions when the atoms move along the [001], [110], [111] directions. The calculation was performed using the initial cubic cell with a lattice constant, $a = 3.945 \text{ \AA}$ at 0 K. The eigenvector is chosen as $e_{\text{Ba}} = 0$, $e_{\text{Ti}} = 0.448$, $e_{\text{O}_I} = -0.75$, $e_{\text{O}_{II}} = e_{\text{O}_{III}} = -0.338$. It can be seen that the rhombohedral [111] distortion has the lowest energy, whereas the strained tetragonal [001] distortion has the highest energy. This result is consistent with the prediction of other theories and experimental fact that there are several structural phase transitions in BaTiO₃ with lowering temperature: from cubic to tetragonal, tetragonal to orthorhombic, and orthorhombic to rhombohedral structures (see, Xu 1991).

Figure 5 illustrates the band structure of BaTiO₃ along high-symmetry directions of the irreducible Brillouin zone. The conduction band, composed primarily of unoccupied Ti 3d states, has a full width of about 10 eV and may be divided into two distinct groups. These two

Table 2. The charge on site of atom Ba, Ti, O in a unit cell of BaTiO₃ (cubic phase).

	Z_{Ba}	Z_{Ti}	Z_{O}	Reference
Nominal	+2	+4	-2	
Empirical model				
	+2.00	+1.88	-1.29	Michel-Calendini <i>et al</i> (1980)
	+1.86	+3.18	-1.68	Khatib <i>et al</i> (1989)
	+1.48	+1.86	-1.11	Turik and Khasabov (1988)
First-principles				
	+2.00	+2.89	-1.63	Cohen and Krakauer (1990)
	+2.12	+2.43	-1.52	Xu <i>et al</i> (1990)
	+1.39	+2.79	-1.39	Xu <i>et al</i> (1994)
SCTB →	+1.72	+2.40	-1.37	This work

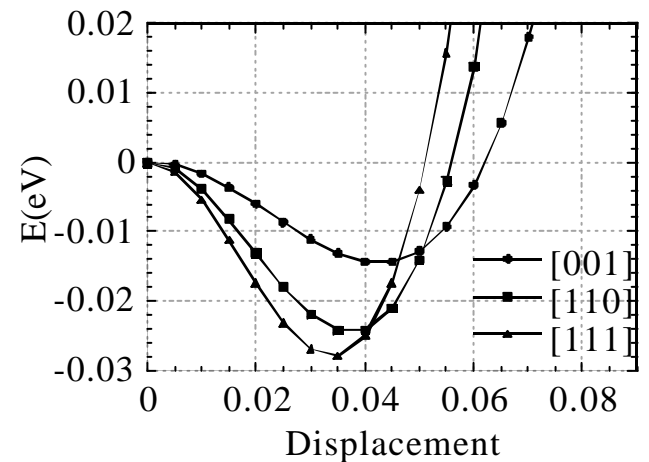


Figure 4. Energy dependence on the atom displacements (in unit of lattice constant, $a = 3.945 \text{ \AA}$)

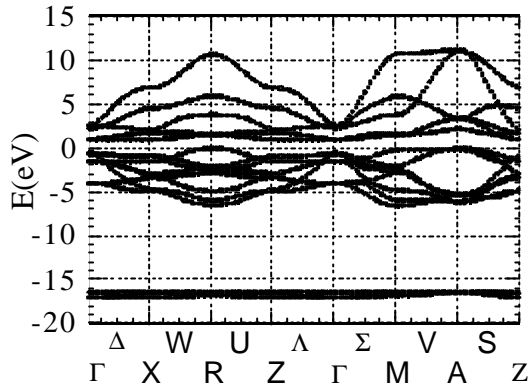


Figure 5. Band structure for BaTiO₃ along high-symmetry directions. The valence-band maximum is taken as the energy zero.

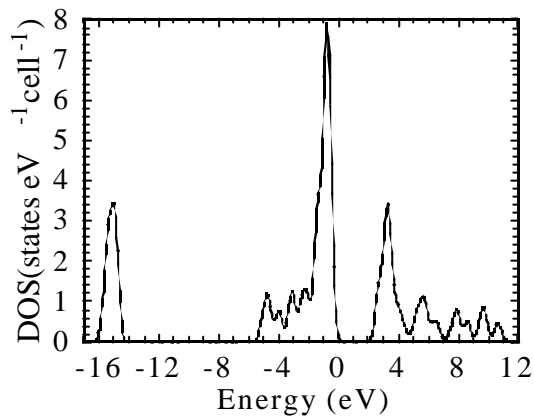


Figure 6. Density of states for BaTiO₃.

groups are reminiscent of the crystal-field splitting of the Ti 3d states into the triply degenerate, t_{2g} , and doubly degenerate, e_g , states. The lower group of states, the t_{2g} band, has a bandwidth of 2.5 eV. The upper group associated with states of e_g have a width of 8 eV. The distance between these two groups is about 1.5 eV. A line with contribution of Ba 6s state mixes these two groups with each other. The simple band structure given here has the main feature like Kohn–Sham electronic band for BaTiO₃ (see also Ghosez *et al* 1998).

The density of states (DOS) is plotted in figure 6. According to our identification the deepest peak belongs to oxygen 2s band. The lower valence band is formed mainly from 2p oxygen band. The following lower and upper conduction bands came from t_{2g} and e_{2g} titanium orbitals mixed with Ba 6s orbital. The valence band maximum was taken as zero energy.

3. Conclusion

Using a limited set of parameters, personal computer and self-consistent tight binding method, we can calculate some characteristics of BaTiO₃ such as total energy, lattice constant, density of state, band structure etc which are in agreement with the results of other methods.

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