

AB INITIO MODELING OF ELECTRON SUBSYSTEM OF MULTIATOMIC CRYSTALS: SOFTWARE PACKAGE

BABA GASIMOV¹

ABSTRACT. A software package developed by the author is based on concepts of microscopic solid state theory and provides ab initio calculation of some fundamental aspects of multiatomic crystals. Results for *BaTiO₃*, *PbMoO₄*, and *GeTe* are in good agreement with available published experimental data.

Keywords: numerical modelling, band structure calculation, ferroelectric phase transition, pseudopotential method, total energy calculation.

AMS Subject Classification: 92F05, 34-04, 34G20.

1. INTRODUCTION

This work deals with an application of modern methods and concepts of microscopic solid state theory as based on ab initio uniform approach to numerical modelling of electron subsystem of crystalline solids and performing total energy calculations.

A software package was created to facilitate research related to band calculations, total energy per unit cell, crystal binding energy analysis. This package called “SCPPBAND” for Self-Consistent Pseudopotential Band calculation, enables the study of the influence of electron energy spectrum details on lattice stability, and thereby predicts condition for crystal phase transition.

In an earlier works [1,7] the author developed ab initio numerical model for the description of the phonon subsystem of crystals as well as its application for the calculation of anisotropic resistivity of hexagonal closed packed metals under pressure.

2. TECHNIQUE AND FORMULAS

The algorithm used in the package is based on the solution of the Schrodinger equation for the band problem

$$H\Psi_k^n(\mathbf{r}) = E_n(\mathbf{k})\Psi_k^n(\mathbf{r}), \quad (1)$$

where n is the band number, \mathbf{k} is the Brillouin zone (BZ) vector. In the pseudopotential method, the wave function $\Psi_k^n(\mathbf{r})$ in (1) is expanded in plane waves (PW) that leads to the equation for defining the band structure

$$\sum_{GG'} (H_{GG'}(\mathbf{k}) - E(\mathbf{k})\delta_{GG'}) a_G^n(\mathbf{k}) = 0. \quad (2)$$

In this case the Hamiltonian can be defined by superposition of screened ionic pseudopotentials

¹Qafqaz University, Baku, Azerbaijan,
e-mail: Baba_qasimov@box.az
Manuscript received September 2012.

$$H=T+V_{ps}(\mathbf{r}), V_{ps}(\mathbf{r}) = \sum_{l=1}^N \sum_{\alpha=1}^{NTP} \sum_{i=1}^{N_{\alpha}} V_{\alpha}(\mathbf{r} - \mathbf{R}_i). \quad (3)$$

The common expression for screened pseudopotential form-factor has the form

$$\mathbf{V}_{GG'}(\mathbf{k}) = \sum_{\alpha=1}^{NTP} S_{\alpha}(\mathbf{G}' - \mathbf{G}) F_{\alpha}(\mathbf{k}, \mathbf{G}, \mathbf{G}'), \quad (4)$$

$$F_{\alpha}(\mathbf{k}, \mathbf{G}, \mathbf{G}') = \Omega^{-1} \iiint \exp[-i(\mathbf{k}+\mathbf{G})\mathbf{x}] V_{\alpha}(\mathbf{x}) \exp[i(\mathbf{k}+\mathbf{G}')\mathbf{x}] dx, \quad (5)$$

$$S_{\alpha}(\mathbf{G}-\mathbf{G}') = \sum_{i=1}^{N_{\alpha}} \exp[i(\mathbf{G}-\mathbf{G}')\mathbf{R}_i]. \quad (6)$$

The set (2-6) defines a secular equation in the pseudopotential method for no symmetrical plane wave (PW) basis.

In order to take into the account of the crystal symmetry it would be convenient to represent the wave function as the symmetrized combination of plane waves (SPW)

$$\Psi_k^n(r) = \sum_i a_i^n(k) \cdot SPW_i. \quad (7)$$

Such decomposition reflects symmetry properties of the crystal under consideration by using projection operator technique [13].

Here, the symmetrized basis is constructed in such a way that the computer memory retains no more than one matrix element of multidimensional irreducible representation (IR). All the rays of K-star are thereby considered as a prototype, whereas the fixed matrix element of multidimensional IR is a projection operator.

Not all the original PWs contribute to SPW basis in symmetrising the secular equation which significantly reduces the size of the secular matrix. It is crucial that in expression (5) the second exp term can be replaced by SPW, whereas the first exp term may be left unchanged thereby reducing the amount of computation [22].

Thus, Hamiltonian matrix elements can be written in the following form

$$\begin{aligned} H_{ij} &= \int_V PW_i(\hat{H}) SPW_j d\mathbf{r} = A_i^n A_j^n \int_V PW_i(\mathbf{Q}_1^S) (\hat{H}) \left\{ \sum_l^{N_i^S} C_j(l) PW_j(\mathbf{Q}_l^S) \right\} d\mathbf{r} = \\ &= A_i^n A_j^n \sum_l^{N_j^S} C_j(l) \int_V PW_i(\hat{H}) PW_j d\mathbf{r}. \end{aligned} \quad (8)$$

The pseudopotential method basic quantity to provide self-consistency in density functional approximation is the valence charge density

$$\rho(\mathbf{r}) = \sum_{k \in BZ} W(\mathbf{k}) \sum_{\alpha=1}^{NIR} \sum_n \left| \sum_G a_G^n(\mathbf{k}) SPW_G \right|^2. \quad (9)$$

Here, $W(\mathbf{k})$ is the weight factor of the BZ point. Using the special points method, we can integrate over BZ and calculate the values of $\rho(\mathbf{r})$ on the grid points of the unit cell. The function $\rho(\mathbf{r})$ is used then to calculate the Fourier transform of $\rho(\mathbf{G})$ via fast discrete orthogonal

Fourier transformation. Further Fourier components of charge density are used to calculate the screening potential in the reciprocal space

$$V_{scr}(G) = V_H(G) + V_{ex}(G), \quad (10)$$

where V_H is the Hartree electrostatic potential, $V_{ex}(\mathbf{G})$ is the exchange potential in Slater approximation. The potential (10) is used for the additive screening of ionic pseudopotential form-factor in the selfconsistency procedure. In this case, a partial mixing of the input potential from a previous iteration is applied to accelerate convergence

$$V_{in}^{i+1} = (1 - \beta)V_{in}^i + \beta V_{out}^i. \quad (11)$$

Here, the coefficient β is the mixing coefficient of successive iterations. The general scheme of the procedure is presented in Figure 1.

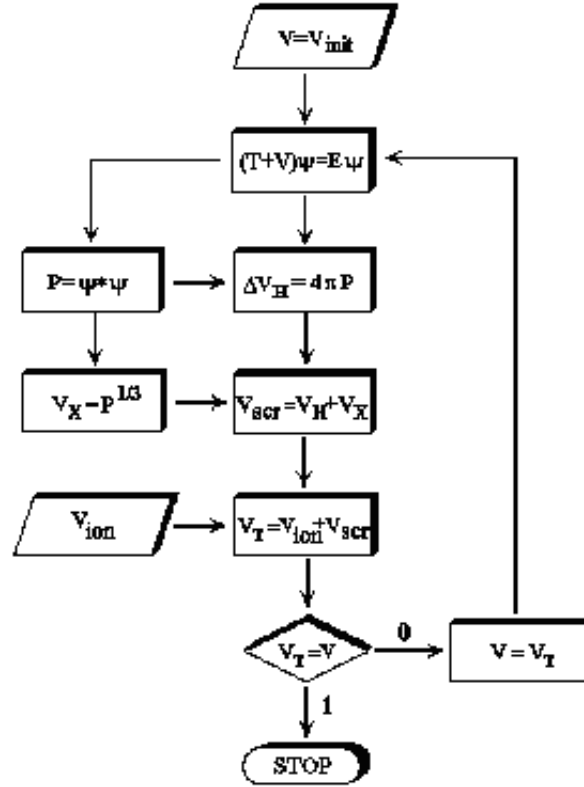


FIGURE 1. The self-consistency procedure

In the local approximation for screened atomic form-factor in accordance with (5) we obtain

$$F_\alpha(\mathbf{k}, \mathbf{G}, \mathbf{G}') = F_\alpha(|\mathbf{G}-\mathbf{G}'|) = \frac{1}{\Omega_{\text{cell}}} \int V_\alpha(\mathbf{x}) \exp[(\mathbf{G}-\mathbf{G}')\mathbf{x}] d\mathbf{x}. \quad (12)$$

Here, V_α is the local pseudopotential for α -type atom in the unit cell, and we use the Ashcroft ionic single-parametric pseudopotential [2, 3], which has the following form in the real space

$$W(r) = \begin{cases} 0, & r \leq R_C \\ -\frac{Z_V}{r}, & r > R_C \end{cases}. \quad (13)$$

The parameters ZV and RC are the ionic charge and core radius, respectively. We denote the ionic pseudopotential by $W(r)$ to emphasise the difference of this value vis-à-vis the atomic pseudopotential $V\alpha$. In order to relate these values, we introduce the screening model of the ionic pseudopotential in the crystal.

Two screening models: dielectric and additive are incorporated into the package. The screened pseudopotential form-factor $V\alpha$ for α type atom enters into band structure calculation via expression (5). In order to provide transferability of the form-factor of a given element in calculations of other compounds, we have to start from the ionic form-factor and then screen it in the environment of the concrete crystal.

The form-factor (12) in local approximation is defined as follows:

$$F_{\alpha}(q) = \frac{W_{\alpha}(q)}{1 + (1 - f(q)) \cdot y_0(q/2/k_F)}, \quad (14)$$

where k_F is the Fermi impulse of screening electron gas, $y_0(x)$ – the Lindhard dielectric function:

$$y_0(x) = \frac{1}{2\pi k_F x^2} \left[\frac{1 - x^2}{2x} \operatorname{Ln} \left| \frac{x + 1}{x - 1} \right| + 1 \right], \quad (15)$$

and $f(q)$ is the correlation function in the Hubbard-Sham form:

$$f(q) = \frac{q^2}{2(q^2 + k_F^2 + k_s^2)}, \quad k_s^2 = 2k_F/\pi. \quad (16)$$

In contrast to the dielectric formalism, the additive screening of the ionic potential is accomplished on the basis of the iterative representation of self-consistency procedure itself. In this case, the screened potential is related to the ionic potential at each step of self-consistency procedure by

$$V(r) = \sum_{\alpha} W(\mathbf{r} - \mathbf{R}_{\alpha}) + V_H(\mathbf{r}) + V_{ex}(\mathbf{r}), \quad (17)$$

where $V_H(r)$ is the Hartree potential, $V_{ex}(r)$ is the exchange-correlation potential in the Slater's $X\alpha$ approximation. Within the pseudopotential method, it is convenient to calculate the expression (17) in reciprocal space. In this case, the final expression for the screened pseudopotential form-factor can be written in the form

$$F(q) = \sum_{\alpha} S_{\alpha}(q) F_{\alpha}^0(q) + V_H(q) + V_{ex}(q). \quad (18)$$

The SCPPBAND software package is capable of performing the calculation of the crystal total energy per unit cell. In the density functional approximation [6, 21], by using of reciprocal space formalism [18], and expanding the Bloch wave functions in the PW basis and switching to the Fourier representation, the total energy in the general case of multi-atomic crystals, can be presented in the form:

$$E_{tot} = \sum_{k, nv} E_{nv}(\mathbf{k}) - \Omega_{\text{cell}} \left\{ \frac{1}{2} \sum_{\mathbf{G} \neq 0} V_H(\mathbf{G}) \rho(\mathbf{G}) + \frac{1}{4} \sum_{\mathbf{G}} V_{xc}(\mathbf{G}) \rho(\mathbf{G}) \right\} + \sum_P \alpha_{1P} \cdot Z_P + 1/2 \cdot \sum_{PP'} M_{PP'} Z_P Z_{P'}. \quad (19)$$

The first term here stands for the contribution of the unit cell electrons. The summation is carried over all valence band electron states. Calculation of this contribution is made by BZ

integration using 3-dimensional spline interpolation over the whole BZ [20]. $Env(\mathbf{k})$ is the electron dispersion law. The expression in brackets represents a correction for electron-electron interaction in which $VH(\mathbf{G})$ and $Vex(\mathbf{G})$ are Fourier components of Hartree and exchange correlation potentials. The value $\alpha 1P$ in the penultimate term is the generalization of the value $\alpha 1$ in [6] for the case of multi-atomic crystals, and presents the atomic pseudopotential electronegativity of p-type related with the kinetic energy compensation in the core region, which is the essence of the pseudopotential theory [19, 5]. This value depends on the sampling of the concrete pseudopotential and compensates for the ambiguity of this choice. In the case of Ashcroft pseudopotential (5), $\alpha 1P$ can be presented in the following form:

$$\alpha_{1P} = \frac{1}{\Omega_{cell}} \int \left(W_P(r) - \frac{Z_P}{r} \right) d^3r = \frac{4\pi Z_P R_C^2}{\Omega_{cell}}. \quad (20)$$

The last term in (19) represents the contribution of the Coulomb interaction of the ionic subsystem to the crystal total energy. MPP' are Madelung constants [23] defined by compound formula, unit cell geometry, and charges of ions in the unit cell. In the SCPPBAND software package the Madelung constants' computation is performed in the general case of multi-atomic crystal.

The current version the SCPPBAND software package consists of 6 basic programs written in FORTRAN 90. Some auxiliary modules are worked out in ASSEMBLER and C. The structure of the software package "SCPPBAND" is given in Figure 2.

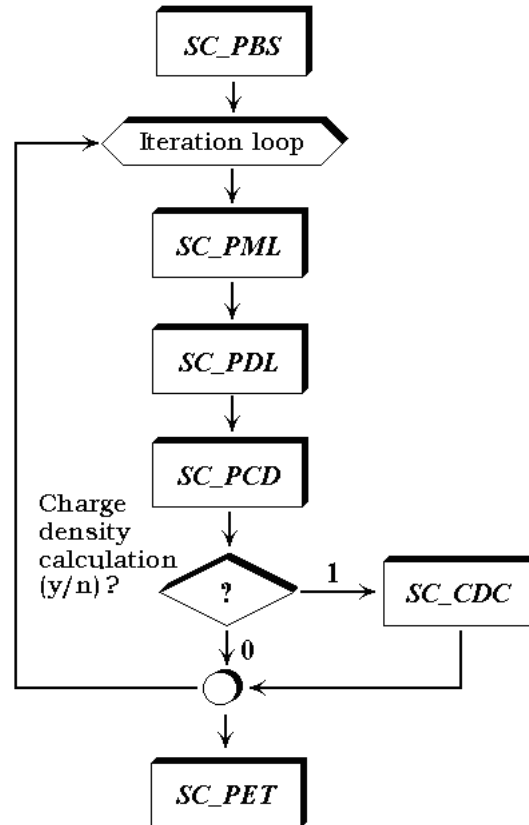


FIGURE 2. The structure of the Software Package "SCPPBAND"

Notations in the above are as follow

<i>SC_PBS</i>	-the SPW basis construction in accordance with space group symmetry of the crystal;
<i>SC_PML</i> (<i>SC_PMN</i>)	-the Hamiltonian matrix elements calculation within the frame of local (nonlocal) pseudopotential method optionally using Lowden perturbation theory to reduce the matrix order;
<i>SC_PDL</i>	-the solution of Sturm - Liouville problem for hermitian complex matrix;
<i>SC_PCD</i>	-the calculation of the electron charge density distribution function in the lattice unit cell and the screening potential construction;
<i>SC_CDC</i>	-the graphical presentation of the electron charge density distribution function, as well as the contour diagrams mapping;
<i>SC_PET</i>	-the calculation of the total energy per unit cell.

For the given crystal structure the module “*SC_PBS*” runs only once. “*SC_PML*”, “*SC_PDL*”, “*SC_PCD*” run in every step of self-consistency process until convergence is reached. As for the module “*SC_PET*” it can be called at each iteration to assure self-consistency dynamics, and then one final time after the convergence is obtained.

3. SPECIFIC APPLICATIONS

The SCPPBAND software package in the current version was applied to perform the calculation of self-consistent pseudopotential band structure and the total energy of multi-atomic crystals. There are no restrictions on symmetry and on the geometrical structure of the crystal. The election energy spectrum calculations were carried out for the curtain BZ symmetry directions, as well as in the general position point. The software package was specifically applied to perform self-consistent band calculations for the *BaTiO3* - perovskite, a representative of wide-gap dielectrics, having space group symmetry *Oh1 (Pm3m)*. The results are in good agreement with the data obtained by the alternative methods *LCAO*, *APW* and *SW- α* except for the deep-filled bands. The latter, however, is explicable within the pseudopotential approach and can be corrected by adding strongly localized states into the PW basis [15, 8].

The SCPPBAND software package was applied for the calculation of the *PbMoO4* crystal that had never before been the object of successive microscopic calculation. The crystal has sheelite-type complicated multi-atomic structure which allows the testing of the effectiveness of the suggested software package, namely, in the case of resource-intensive computations. The calculations enable for the first time the obtaining of the self-consistent band structure of this crystal and to the confirmation quantitatively of the conclusion of the determinative contribution of metal oxygen cluster to the formation of optical spectra for this class of crystals [4, 9].

We have applied the suggested software package to ferroelectric-semiconductor *GeTe*. This yields the first ever calculation of dependence of the total energy on the value of the unit cell static deformation according to various phonon modes, including the soft modes. The dependencies obtained have been used to construct the adiabatic potential and derive the microscopic numerical model of ferroelectric phrase transition in *GeTe* within the vibronic theory. Vibronic structural instability was suggested in [10-12] to be the only source of ferroelectric phase transition in this crystal. Now this conjecture has been confirmed numerically.

The specific applications described above on one hand demonstrate the capabilities of the SCPPBAND software package on other hand investigate compounds which are perspective for creating new materials with preset properties [14, 16, 17].

REFERENCES

- [1] Arkhipov, R.G., Kasumov, B.M., (1980), Calculation of anisotropy of resistivity of HCP metals (USSR, Academy of Sciences, Institute of High Pressure Physics, 25 pp.), Bulletin of All Union Scientific and Technical Information Center, Algorithms and Programs, Collector 1, No.003929, p.53 (in Russian).
- [2] Ashcroft, N.W., (1966), Electron-ion pseudopotential in metals, Phys. Lett., 23, pp.48-51.
- [3] Ashcroft, N.W., Mermin, N.D., (1976), Solid State Physics, Holt, Rinehart and Winston.
- [4] Darvishov, N.G., Kasumov, B.M. et.al., (1993), The part of the cluster MoO₄-2 information of the reflection spectra of PbMoO₄, Baku University News (Physical and Mathematical Sciences), 1, pp.146-148.
- [5] Heine, V., Cohen, M.L., Weaire, D., (1970), The Pseudopotential Concept, Pseudopotential Theory of Cohesion and Structure, Solid State Physics, Advanced in Research and Applications, 24, Academic Press, NY-London.
- [6] Hohenberg, P., Kohn, W., (1964), Inhomogeneous electron gas, Phys. Rev., B136, pp. 864-871.
- [7] Kasumov, B.M., Arkhipov, R.G., (1981), Anisotropic resistivity of HCP metals under pressure, Proc. of the 11-th Annual International Symposium on Electronic Structure of Metals and Alloys, Gaussig, GDR, pp. 215-219.
- [8] Kasumov, B.M., Sharbatov, V.Kh., (1990), Band structure calculation of Perovskites by selfconsistent pseudopotential method, Baku State University Proceedings (Kinetic and Optical Phenomena in Matter), BSU, p.79 (in Russian).
- [9] Kasumov, B.M., Sharbatov, V.Kh., (1995), Energy spectrum of crystals with sheelite structure, 10-th International Conference on Ternary and Multinary Compounds, Stuttgart, September 19-22.
- [10] Kasumov, B.M., Sharbatov, V.Kh., (1996), The GeTe band structure calculation by pseudopotential method, Turkish Journal of Physics, 20, pp.497-499.
- [11] Kasumov, B.M., (1997), Microscopic modeling of ferroelectric phase transition in GeTe by pseudopotential method, Baku University News (Physical and Mathematical Sciences), 1, pp.38-43.
- [12] Kasumov, B.M., (2004), Microscopic model of ferroelectric transition in GeTe crystal, Application of Information-Communication Technologies in Science and Education, Baku, International Conference Theses, p.177-178.
- [13] Kovalev, O.V., (1993), Representation of the Crystallographic Space Groups, 2nd Edition, Gordon and Breach, London, 390p.
- [14] Kwi-Il Park, Minbaek Lee et.al., (2012), Flexible nanocomposite generator made of BaTiO₃ nanoparticles and graphitic carbons, Adv. Mater., 24, p.2999-3004.
- [15] Mamedov, A., Kasumov, B.M., Sharbatov, V.Kh., (1990), Selfconsistent pseudopotential band structure calculation of perovskites: BaTiO₃, Izv. Vyssh. Uchebn. Zaved. Fiz., 1, p.128, (ISSN: 0021-3411, in Russian).
- [16] Mark J.Polking, Myung-Geun Han et.al., (2012), Ferroelectric order in individual nanometer-scale crystals, Nature Materials, 11, pp.700-709.
- [17] Min Shen , Xiaohu Zhang et.al., (2013), Hierarchical PbMoO₄ microspheres: hydrothermal synthesis, formation mechanism and photocatalytic properties, CrystEngComm, 15, p.1146-1152.
- [18] Perdew, J.P., Zunger, A., (1981), Self-interaction correction to density-functional approximations for many-electron systems, Phys. Rev. B - Condensed Matter, 23, pp. 5048-5079.
- [19] Philips J.C., Kleinman L., (1959), New method for calculating wave function in crystals and molecules, Phys. Rev., 116(2), pp. 287-294.
- [20] Qasimov, B.M., (2007), About the 3-dimentional spline interpolation of lattice functions, II International Conference on ICT in Science and Education, Baku, November 1-3, pp.537-539.
- [21] Rose, J.H., Shore, H.B., (1975), Calculation method for the inhomogeneous electron gas, Solid State Communications, 17(3), pp. 327-330.
- [22] Schlosser, H., (1962,) Symmetrized combinations of plane waves and matrix elements of the Hamiltonian for cubic lattices, J. Phys. Chem. Solids, 23, pp. 963-969.
- [23] Tosi, M., (1964), Cohesion Ionic Solids in the Born Model, Solid State Physics, 16, 120p.



Baba Gasimov is an associate professor at Qafqaz University in Baku. He graduated from Moscow State University with honor in 1976. He obtained his Ph.D. degree in Physics from Moscow State University in 1981 and academic title of Senior Scientific Researcher in 1994. He has published more than 40 research articles and monographs. His research interests include mathematical modeling of molecular systems and solids.