

# ON THE CRITERION OF THE CONSTRUCTION OF A LOCAL MODEL POTENTIAL FOR SILICON

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The electron energy band spectra of silicon have been calculated by using an analytic approximant of the total atomic potential in the direct space with regard for a finite size of a model Coulomb well in a vicinity of the atomic nucleus. The band energies have been evaluated in a wide range of the single parameter  $\beta$  defining the well depth. The approximate criterion for the choice of  $\beta$  for silicon has been obtained. The Hamiltonian matrix has been calculated within the mixed basis (MB) of one-particle states consisting of core Bloch functions and plane waves. The reasons for a considerable dispersion of the band energies calculated with different pseudopotentials justified in the density functional theory are qualitatively established.

## 1. Introduction

Values of the band energies of electrons in semiconductor crystals obtained by different authors by the method of local electron density functional (LDA) indicate a significant dispersion [1, 2]. Especially, this concerns the results obtained by the solution of the Kohn–Sham one-particle equation in the basis of plane waves with different *a priori* atomic pseudopotentials [3,4]. The last ones differ from one another by values of the radii  $r_l$  ( $l = s, p, d$ ), i.e. by the distances from the atomic nucleus, at which the local part of a pseudopotential equals the corresponding potential which acts on an electron in the state  $l$  at points  $r \geq r_l$ . The choice of radii  $r_l$  is physically unjustified. Each collection of  $r_l$  corresponds to own pseudopotentials. In particular, hard [3], soft [4], and ultrasoft [5] pseudopotentials are characterized, respectively, by small, intermediate, and great values of  $r_l$ . Thus, we deal with the well-known phenomenon of the multiplicity of pseudopotentials [6]. The quantitative criterion for the differences between hard, soft, and ultrasoft pseudopotentials consists in the difference of the corresponding depths of potential wells  $W_l(r = 0)$ . Possibly, it is one of the reasons for quantitative differences of the parameters of the electron energy spectrum obtained on their basis under otherwise equal conditions, i.e. for the same exchange-correlation

potentials, the identical numbers of plane waves in the basis, etc.

The goal of this work is to study the sensitivity of the band energies to the choice of a model of the potential of a crystal, in particular to the depth of a model Coulomb potential well. We will illustrate this dependence by the direct calculation with the use of a mixed basis [7,8]. This allows us to explain simultaneously the dispersion of the band parameters which are obtained with the help of different pseudopotentials, though their theoretical base is practically common. In addition, we mention the increasing interest in the approaches which are based on potentials in the direct space in the connection with the investigation of nanostructures [9]. Just such potentials are used in calculations in the present work.

## 2. Model Potential

The potential of a crystal which acts at a site of the lattice  $\mathbf{c}$  is a superposition of one-site terms

$$v(\mathbf{r} - \mathbf{c}) = \sum_{\mathbf{C}} v(\mathbf{r} - \mathbf{c} - \mathbf{C}), \quad v(\mathbf{r}) = \\ = v_n(\mathbf{r}) + v_e(\mathbf{r}) + v_{xc}(\mathbf{r}), \quad (1)$$

i.e. the sum of the potentials of nuclei  $v_n$ , electrons  $v_e$ , and exchange-correlation potential  $v_{xc}$ . We replace the Coulomb potential of a nucleus  $v_n(r) = -A/r$  which is divergent on the site by the approximate expression

$$v_{na}(r) = -A \operatorname{erf}(\sqrt{p}r)/r, \quad v_{na}(0) = -2A\sqrt{p}/\pi. \quad (2)$$

That is, we replace the Coulomb potential  $v_n$  by the potential well with depth  $v_{na}(0)$  which depends on the nucleus charge  $A$  and the parameter  $p$ . The potential  $v_{na}$  takes the Coulomb form under the condition  $\operatorname{erf}(\sqrt{p}r) = 1$  which is satisfied with high accuracy for  $r \geq 2/\sqrt{p}$ . Increasing  $p$ , we reduce the interval  $0 \leq r \leq 2/\sqrt{p}$ , where  $v_{na}$  differs from the Coulomb potential.

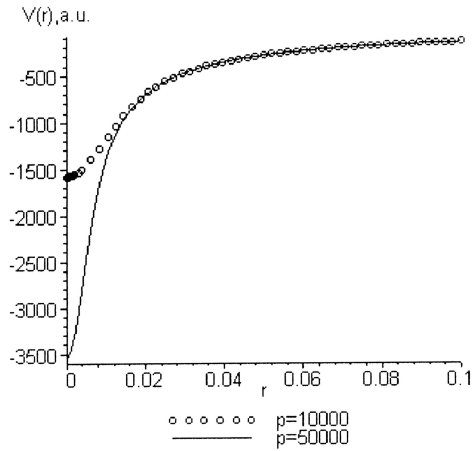


Fig. 1. Model Coulomb potentials of a nucleus of Si for small values of the well depth

In Fig. 1, we show the curves of the model potential (2), for which the Coulomb behavior is revealed at distances from the nucleus  $r \geq 0.01$  a.u. Such potentials do not ensure, as will be shown below, the correct values of the energies of electrons in all bands.

In Fig. 2, we give the curves of the model potential (2), for which the Coulomb behavior is revealed at distances from the nucleus  $r \geq 0.0001$  a.u. Such potentials ensure, as will be shown below, the correct values of the energies of electrons in all bands. To what extent is the model potential

$$v(r) = v_{na}(\mathbf{r}) + v_e(\mathbf{r}) + v_{xc}(\mathbf{r}) \quad (3)$$

suitable for the calculation of the electron energy spectrum of crystals?

We seek the electron energy spectrum of a crystal by using the Schrödinger equation

$$(T + V(\mathbf{r}))\Psi_{\mathbf{k}\alpha}(\mathbf{r}) = E_{\mathbf{k}\alpha}\Psi_{\mathbf{k}\alpha}(\mathbf{r}), \quad (4)$$

in which  $T = -\nabla^2/2$  is the operator of kinetic energy,  $V$  is the potential acting on an electron in the crystal,  $\Psi$  is the eigenvector, and  $E$  is the eigenvalue of the energy at the point  $\mathbf{k}$  of the Brillouin zone in the energy band with number  $\alpha$ . The wave function of an electron in the crystal is sought in the mixed basis:

$$\Psi_{\mathbf{k}\alpha}(\mathbf{r}) = \sum_t \sum_{\mathbf{d}} a_{\mathbf{k}t\mathbf{a},\alpha} |\mathbf{k}t\mathbf{a}\rangle + \sum_{\mathbf{G}} a_{\alpha}(\mathbf{k} + \mathbf{G}) |\mathbf{k} + \mathbf{G}\rangle, \quad (5)$$

where  $a$  are the variational coefficients of the expansion in Bloch core states

$$|\mathbf{k}t\mathbf{a}\rangle = N^{-1/2} \sum_{\mathbf{D}} e^{i\mathbf{k}(\mathbf{a}+\mathbf{A})} \varphi_t(\mathbf{r} - \mathbf{a} - \mathbf{A}) \quad (6)$$

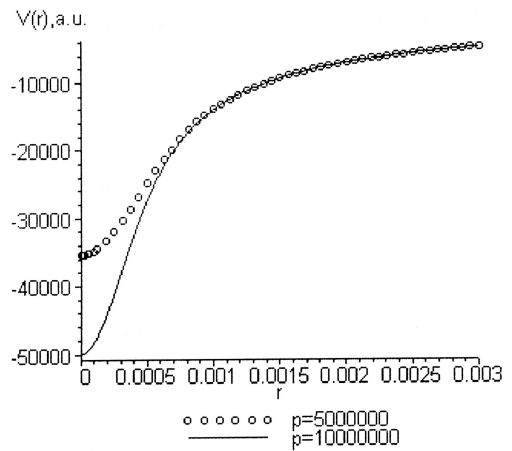


Fig. 2. Model Coulomb potentials of a nucleus of Si for great values of the well depth

and in plane waves

$$|\mathbf{k} + \mathbf{G}\rangle = \Omega^{-1/2} \exp(i(\mathbf{k} + \mathbf{G})\mathbf{r}). \quad (7)$$

Here,  $t = \{nlm\}$  are the quantum numbers of states of the core,  $\mathbf{a}$  are the coordinates of an atom in the elementary cell,  $\mathbf{G}$  is a vector of the reciprocal lattice,  $N$  is the number of elementary cells in the crystal,  $\mathbf{A}$  are vectors of the Bravais lattice,  $\varphi$  are the wave functions of electrons of the atomic core [11], and  $\Omega$  is the crystal volume.

Substituting (5) in (4), we get the block system of linear homogeneous equations

$$\begin{pmatrix} H_{\mathbf{k}t\mathbf{d},\mathbf{k}t'\mathbf{d}'} - ES_{\mathbf{k}t\mathbf{d},\mathbf{k}t'\mathbf{d}'} & H_{\mathbf{k}t\mathbf{d},\mathbf{k}+\mathbf{G}'} - ES_{\mathbf{k}t\mathbf{d},\mathbf{k}+\mathbf{G}'} \\ H_{\mathbf{k}+\mathbf{G},\mathbf{k}t'\mathbf{d}'} - ES_{\mathbf{k}+\mathbf{G},\mathbf{k}t'\mathbf{d}'} & H_{\mathbf{k}+\mathbf{G},\mathbf{k}+\mathbf{G}'} - E\delta_{\mathbf{G},\mathbf{G}'} \end{pmatrix} \times \begin{pmatrix} a_{\mathbf{k}t\mathbf{d},\alpha} \\ a_{\alpha}(\mathbf{k} + \mathbf{G}) \end{pmatrix} = 0, \quad (8)$$

in which  $H_{\alpha\beta}$  are the matrix elements of the Hamiltonian,  $S_{\alpha\beta}$  is the overlap matrix on a mixed basis, and  $a$  are the variational coefficients. In order to solve the system of equation (8), it is necessary to deduce the formulas for elements of the matrices  $S$  and  $H$ . The Hamilton operator  $H = T + V$ , where  $T$  and  $V$  are the operators of kinetic and potential energies, respectively. We approximate the latter by the following formula:

$$V(r) = \sum_{i=1}^{20} c_i e^{-p_i r^2} + e^{-\alpha r^2} \left( \frac{\text{erf}(\sqrt{\beta}r)}{r} - \frac{\text{erf}(\sqrt{\gamma}r)}{r} \right), \quad (9)$$

in which the coefficients  $c_i, p_i$  determine the long-range “soft” part of the potential of an atom, and  $\alpha, \beta$ , and  $\gamma$  correspond to the “hard” component localized in the vicinity of the atomic nucleus. The matrix elements of the first term in (9) are obtained analytically [10]. We determined the matrix elements of the second term in (9) with the help of the integral representation

$$\frac{\text{erf}(\sqrt{p}r)}{r} = \frac{2}{\sqrt{\pi}} \int_0^{\sqrt{p}} \exp(-t^2 r^2) dt \quad (10)$$

and the integration over the coordinates and the variable  $t$ .

We take the wave functions in the form of Cartesian Gaussians [11]

$$\varphi_{nem}(\mathbf{r} - \mathbf{A}) = \sum_i c_i N_i (x - A_x)^l (y - A_y)^m (z - A_z)^n \times \exp(-\alpha_i (\mathbf{r} - \mathbf{A})^2). \quad (11)$$

### 3. Matrix Elements of the Potential

The matrix elements of the first term in (9) on the Bloch functions of the  $s$ -symmetry centered at the lattice sites  $\mathbf{a}, \mathbf{b}$  with coordinates  $\mathbf{B}$  are determined by the formulas

$$\langle s\mathbf{ka} | V(\mathbf{r} - \mathbf{c} - \mathbf{C}) | s\mathbf{kb} \rangle = QGF, \quad (12)$$

where  $Q$  is the structural factor,

$$Q = \exp(-i\mathbf{ka} + i\mathbf{kb} + i\mathbf{kB}), \quad (13)$$

$G$  is the function which defines the diminution of a matrix element in the coordinate space,

$$G = \exp(-\alpha_i \alpha_j (\mathbf{B} + \mathbf{b} - \mathbf{a})^2 / s_{ij}), \quad s_{ij} = \alpha_i + \alpha_j, \quad (14)$$

$F$  is the function which depends on the centering coordinates of wave functions and potentials,

$$F = (\pi/s_{ij})^{3/2} \text{erf}(s_{ij}^{1/2} |\mathbf{D} - \mathbf{c} - \mathbf{C}| t_{\max}) / |\mathbf{D} - \mathbf{c} - \mathbf{C}|,$$

$$D = (\alpha_i \mathbf{a} + \alpha_j (\mathbf{b} + \mathbf{B})) / s_{ij}. \quad (15)$$

The matrix elements of the second term in (9) on the Bloch functions  $s$  and plane waves look as

$$\begin{aligned} \langle s\mathbf{ka} | V(\mathbf{r} - \mathbf{c} - \mathbf{C}) | \mathbf{k} + \mathbf{G} \rangle &= \\ &= \pi/\alpha_i \exp(t_0 \sqrt{\pi} \text{erf}((-t_2)^{1/2} t_{\max}) / (-t_2)^{1/2}), \end{aligned} \quad (16)$$

where

$$t_0 = -\frac{1}{4} (-4i\alpha_i \mathbf{G}\mathbf{a} + (\mathbf{k} + \mathbf{G})^2) / \alpha_i,$$

$$t_2 = -\frac{1}{4} (4i\alpha_i \mathbf{G}\mathbf{a} - 4i\alpha_i \mathbf{G}\mathbf{c} + 4\alpha_i^2 (\mathbf{a} - \mathbf{c} - \mathbf{C})^2 -$$

$$-(\mathbf{k} + \mathbf{G})^2 + 4i\alpha_i \mathbf{k}(\mathbf{a} - \mathbf{c} - \mathbf{C})) / \alpha_i,$$

$$t_{\max} = (\beta_j / (\alpha_i + \beta_j))^{1/2}. \quad (17)$$

The results of calculations are given in Table 1. The band energies of electrons at the point  $\Gamma$  of the Brillouin zone are calculated with different values of the parameter  $\beta$ . The larger the  $\beta$ , the deeper is the potential well. The counting origin for the energy is chosen at the top of the valence band.

**Table 1.** Values of the band energies in Si at the point  $\Gamma$  which depend on  $\beta$ . The degeneration multiplicity is given in the parentheses near the number of a band

Number of a band $i$	$\beta$							
	$1.0 \times 10^4$	$5.0 \cdot 10^4$	$1.0 \times 10^5$	$2.5 \times 10^5$	$1.0 \times 10^6$	$2.0 \times 10^6$	$5.0 \times 10^6$	$1.0 \times 10^7$
	$E_i, \text{eV}$							
1	-1706.96	-1750.42	-1757.7	-1762.22	-1765.08	-1765.59	-1765.63	-1765.59
2	-127.92	-130.09	-130.56	-130.67	-131.04	-131.17	-130.99	-130.90
3 (3)	-88.21	-88.20	-88.32	-88.19	-88.43	-88.54	-88.34	-88.26
4	-11.49	-11.64	-11.68	-11.68	-11.71	-11.71	-11.71	-11.72
5 (3)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
6 (3)	2.90	2.89	2.89	2.91	2.89	2.88	2.88	2.88
7	4.29	3.94	3.84	3.83	3.74	3.68	3.74	3.76
8 (2)	8.02	8.02	8.03	8.00	8.05	8.05	8.03	8.01
9	8.45	8.31	8.27	8.41	8.23	8.27	8.25	8.24
10 (3)	11.72	11.69	11.68	11.77	11.69	11.70	11.69	11.67

It is seen from Table 1 that the positions of the bottom  $\Gamma_1(E_4)$  and the top  $\Gamma_{25}(E_5)$  of the valence band, as well as the bottom of the conduction band  $\Gamma_{15}(E_6)$ , are practically adequate in a wide range of values of the parameter  $\beta$ . However, values of the energy of the level  $E_{1s}(E_1)$  are very sensitive to a change of  $\beta$ . They are stabilized beginning from  $\beta = 2.0 \times 10^6$ . For the level  $E_{2s}(E_2)$ , the dependence on  $\beta$  is noticeable, whereas it is slight for  $E_{2p(3)}$ . This is explained by the fact that the screening of the Coulomb potential is smallest for  $1s$ -electrons. The attractive potential of the nucleus acting on  $2s$ -electrons is screened by  $1s$ -electrons which are closer to the nucleus, and the Coulomb potential of the nucleus acting on  $2p$ -electrons is screened by the repulsive potential of  $1s$ - and  $2s$ -electrons. As seen from Table 1, the model potential (3) with  $\beta = 1.0 \times 10^7$  ensures the stabilization of the energy spectrum of Si in all bands.

The comparison of the results of our calculations with those of other authors and experiments is given in Table 2. For all results, the used methods are based on the common base of the local electron density functional.

Our values of the electron energies of Si at the high-symmetry point  $\Gamma$  presented in Table 2 were calculated in MB. The results of other authors were obtained with the help of the norm-preserving pseudopotential on plane waves (PW) and localized orbitals (LO) [12], with a correction of the self-action (SIC-LDA) [13], with screened exchange (sX-LDA) [14], with optimized effective potential (KLI) [15], method LMTO [16], and the experimental data are taken from [13]. The data given in Table 2 confirm the reality of the approach with MB, and the differences of the band energies calculated within LDA from the experimental data are characteristic of semiconductors and dielectrics [18].

#### 4. Discussion of Results and Conclusions

For small values of the parameter  $\beta$  ( $10^4$ ,  $5 \times 10^4$ ), the corresponding depths of model Coulomb wells are 1542.52 and  $-3495.17$  a.u., respectively. The last ones are much greater than the energy of the atomic level of Si,  $E_{1s} = -68.812$  a.u., but they cannot ensure the

**Table 2.** Band energies of Si (in eV) calculated in this work, by other authors, and experimental data

$i$	Method							
	PW	LO	SIC-LDA	sX-LDA	KLI	LMTO	MB	Exp.
4	-11.95	-11.72	-11.89	-12.47	-11.88	-11.87	-11.72	-12.5
5(3)	0	0	0	0	0	0	0	0
6(3)	2.54	2.64	2.54	3.37	2.86	2.59	2.88	3.05
7	3.39	3.51	3.41	—	3.88	3.88	3.76	4.1

correct values of the band energies of electrons in all bands. To a less extent, this concerns values of the energies of direct gaps (i.e. the distances between the top of the valence band taken as the counting origin for the energy of electrons and the bottom of the conduction band) which coincide to within 0.01 eV for all values of the parameter  $\beta$ . Values of the parameter  $\beta = 10^5$ ,  $2.5 \times 10^5$  correspond to the depths of model Coulomb wells equal to  $-4958.33$  and  $-7861.44$  a.u., respectively, and values of the band energies approach essentially the correct ones. A further increase of the parameter  $\beta$  to  $10^6$  gives a model Coulomb well depth equal to  $-15760.1$  a.u. But it is also insufficient in order to obtain the band energies of electrons in all bands to within 0.01 eV, though the levels of the populated valence band are already quite exact. A further increase of the parameter ( $\beta = 2 \times 10^6$ ,  $5 \times 10^6$ , and  $10^7$ ) gives the depths of model Coulomb wells equal to  $-22303.6$ ,  $-35286.6$ , and  $-49918.3$  a.u., for which the band energies of electrons are stabilized. For four last greatest depths of the wells, the ratios of their values to the energy of the atomic level  $E_{1s}$  in Si are 229, 324, 513, and 725. In this case, the values of the energy levels of electrons are practically identical in all bands, and a further increase of the parameter  $\beta$  does not lead to a significant change in the calculated electron energy spectra. Thus, the approximate criterion of the choice of this parameter for Si is the condition  $v_{na}(0)/E_{1s} \geq 229$ , whereas it is somewhat stronger for diamond, for which  $v_{na}(0)/E_{1s} \geq 300$  [17].

The results of calculations of the band energies of electrons by the mixed-basis method for a wide range of values of the depths of model Coulomb potential wells allow us to conclude that a significant dispersion of values of the energies obtained with various pseudopotentials is mainly conditioned by the differences of the depths of potential wells.

We should like to indicate the advantages of the mixed-basis method. The Bloch localized functions inherent in MB allow one to essentially decrease the number of plane waves in expansion (5). For example, the results given in Table 1 are derived from the system of equations (8), where the size of the matrix for Si equals 951 (941 plane waves and 10 localized functions). The values of the band energies calculated in [12] with the use of atomic *a priori* pseudopotentials are somewhat worse than those obtained by us. However, the size of the secular matrix in [12] has the order of about  $10^5$ , and such a problem should be solved on a supercomputer. The mixed-basis method deals with a true wave function, on the basis of which one can

calculate dipole matrix elements. But this cannot be performed with pseudowave functions used in [12] and in related approaches, because there exists no transition from a pseudowave function to a wave one [6,18]. The core states included in (5) allow one to execute the calculations of the intensity of core-valence luminescence [19], which is also beyond the scope of pseudopotential methods. The mixed-basis method proposed by us has no symmetry limitations characteristic of the methods, in which the muffin-tin potential is used [16].

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#### ПРО КРИТЕРІЙ ПОВУДОВИ ЛОКАЛЬНОГО МОДЕЛЬНОГО ПОТЕНЦІАЛУ КРЕМНІЮ

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#### Резюме

Розраховано електронні енергетичні спектри кремнію за допомогою аналітичної апроксимації повного потенціалу атома у прямому просторі, яка враховує скінченність модельної кулонової ями в околі ядра атома. Досліджено залежність розрахованих зонних енергій від єдиного параметра  $\beta$ , який визначає глибину ями. Розрахунки зонних енергій електронів проведено з різними значеннями цього параметра. Отримано наближений критерій вибору величини  $\beta$  для кремнію. Матрицю гамільтоніана розраховано у змішаному базисі одночастинкових станів, що складається з функцій Блоха атомних серцевин і плоских хвиль. За допомогою різних псевдопотенціалів, обґрунтованих у теорії функціонала повної електронної густини, якісно встановлено причини дисперсії розрахованих параметрів електронних енергетичних зон.