

Application of Keating's valence force field model to non-ideal wurtzite materials

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Abstract

We discuss the application of Keating's valence force field model to non-ideal wurtzite materials such as GaN, InN and AlN.

1. Introduction

Strains have significant effects on the electronic and optical properties of lattice-mismatched semiconductor heterostructures such as quantum dots or nanowires. They indeed shift the conduction and valence band edges [1] and might give rise to piezoelectric fields [2], which tend to separate the electrons from the holes [3, 4]. In inhomogeneous systems, the strains $\varepsilon_{\alpha\beta}$ can be conveniently computed with continuum elasticity theory [5, 6], which is believed to hold down to nanometer-size systems [7]. These strains can then be used directly as input for electronic structure calculations within the effective mass or $\mathbf{k} \cdot \mathbf{p}$ approximations [8, 9], which are also continuous medium theories. The strains $\varepsilon_{\alpha\beta}$ do not, however, provide enough information for atomistic electronic structure methods such as tight-binding [10, 11] or pseudopotentials [12, 13], which need atomic positions as input. Indeed, the atomic positions can hardly be reconstructed from the strains, whose analytic structure is very complex around, e.g., surfaces and interfaces, and which do not characterize the *internal* strains [14] within the unit cell (i.e., the motion of one sublattice with respect to the other). Therefore, the atomic positions used as input for such methods

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are usually computed with semi-empirical force fields such as Keating’s Valence Force Field (VFF) [15], Tersoff [16] or Stillinger-Weber potentials [17].

There is a clear trade-off between the range and complexity of these force fields and their transferability. In the elastic limit (no plastic relaxation), Keating’s VFF model provides a good balance between accuracy and efficiency. This first nearest neighbor force field has originally been developed for diamond and zinc-blende materials [15]. It gives an excellent account of the elastic properties of silicon and germanium, and a reasonable description of those of III-V materials. The latter can be improved with the introduction of long-range interactions arising from the charge transfer between anions and cations [18], at the expense of a larger computational cost. In principle, Keating’s VFF model can also be applied to wurtzite materials. To our knowledge, the relations between the macroscopic elastic constants c_{ij} and Keating’s bond-bending and bond-stretching constants have only been established for “*ideal*” wurtzite materials with equal bond lengths and angles [19, 20]. This is, again, certainly sufficient for the calculation of the strains, but not for the calculation of the input positions of atomistic electronic structure methods, where non-ideality controls the splitting between the highest valence bands [21]. In this paper, we derive the relations between the c_{ij} ’s and Keating’s bond-bending and bond-stretching constants for *arbitrary* wurtzite structures (Section 2). We then apply this model to GaN, AlN and InN, and discuss the strains in a GaN/AlN quantum dot as an example (section 3).

2. The Valence Force Field model of Keating

The valence force field model of Keating has originally been introduced for diamond and zinc-blende materials [15]. The elastic energy per atom reads in this approximation:

$$U_i = \frac{3\alpha}{16r_0^2} \sum_{j=1}^4 (\mathbf{r}_{ij}^2 - r_0^2)^2 + \frac{3\beta}{8r_0^2} \sum_{j=1}^4 \sum_{k>j}^4 \left(\mathbf{r}_{ij} \cdot \mathbf{r}_{ik} + \frac{r_0^2}{3} \right)^2,$$

where \mathbf{r}_{ij} is the vector from a given atom i to one of its four nearest neighbors j . The first term accounts for the changes in bond lengths, while the second

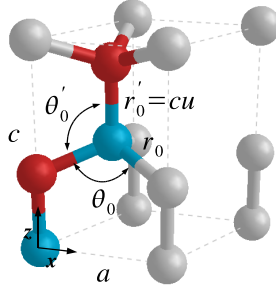


Figure 1: (Color online) The wurtzite unit cell, with the bond lengths r_0 and r'_0 , and the bond angles θ_0 and θ'_0 .

term mostly accounts for the changes in bond angles. The macroscopic elastic constants c_{11} , c_{12} and c_{44} are related to the “bond-stretching” constant α , “bond-bending” constant β and equilibrium bond length $r_0 = a\sqrt{3}/4$ by:

$$c_{11} = \frac{1}{a} (\alpha + 3\beta) \quad (1a)$$

$$c_{12} = \frac{1}{a} (\alpha - \beta) \quad (1b)$$

$$c_{44} = \frac{4}{a} \frac{\alpha\beta}{(\alpha + \beta)}. \quad (1c)$$

Note that the c_{ij} 's are not independent and fulfill the relation $2c_{44}(c_{11} + c_{12}) = (c_{11} - c_{12})(c_{11} + 3c_{12})$. This relation is much better satisfied in group IV diamond materials than in ionic-covalent III-V or II-VI materials where interactions are longer-ranged [18]. It is nonetheless possible to achieve a reasonable description of the elasticity of most semiconductor materials in the above approximation.

In wurtzite materials, the equilibrium length r'_0 of the bonds b' oriented along the c axis is usually different from the length r_0 of the other bonds $\{b\}$. Likewise, the equilibrium angle θ_0 between two b bonds differs from the bond angle θ'_0 between a b and the b' bond (see Fig. 1). r'_0 , r_0 , $\cos\theta'_0$ and $\cos\theta_0$ can

be related to the lattice parameters a , c and u of the material:

$$r'_0 = cu \quad (2a)$$

$$r_0 = \frac{\sqrt{3c^2v^2 + 4a^2}}{2\sqrt{3}} \quad (2b)$$

$$\cos \theta'_0 = \frac{-\sqrt{3}cv}{\sqrt{3c^2v^2 + 4a^2}} \quad (2c)$$

$$\cos \theta_0 = \frac{3c^2v^2 - 2a^2}{3c^2v^2 + 4a^2} = \frac{3 \cos^2 \theta'_0 - 1}{2}, \quad (2d)$$

where $v = 1 - 2u$ [$\cos \theta'_0 = \cos \theta_0 = -1/3$ in an ideal wurtzite material with $c = a\sqrt{8/3}$ and $u = 3/8$]. We can therefore generalize Keating's valence force field model as follows:

$$\begin{aligned} U_i &= \frac{3\alpha}{16r_0^2} \sum_{j=1}^3 (\mathbf{r}_{ij}^2 - r_0^2)^2 \\ &+ \frac{3\alpha'}{16r_0'^2} (\mathbf{r}_{i4}^2 - r_0'^2)^2 \\ &+ \frac{3\beta}{8r_0^2} \sum_{j=1}^3 \sum_{k>j}^3 (\mathbf{r}_{ij} \cdot \mathbf{r}_{ik} - r_0^2 \cos \theta_0)^2 \\ &+ \frac{3\beta'}{8r_0r_0'} \sum_{k=1}^3 (\mathbf{r}_{i4} \cdot \mathbf{r}_{ik} - r_0r_0' \cos \theta'_0)^2 \end{aligned} \quad (3)$$

where the b' bond of atom i is assumed to be $j = 4$. For the sake of generality, we have introduced two bond stretching constants α and α' for the b and b' bonds, as well as two bond bending constants β and β' . It is easily verified that the elastic energy is minimum and zero in the unstrained wurtzite lattice.

We shall now relate the macroscopic elastic constants c_{ij} of the material to the microscopic constants α , α' , β and β' . To this end [15], we identify the second-order development of Eq. (3) as a function of strains to the macroscopic elastic energy of the unit cell. We therefore consider a bulk wurtzite crystal with lattice vectors:

$$\begin{aligned} \mathbf{a} &= a(1, 0, 0) \\ \mathbf{b} &= a(1/2, \sqrt{3}/2, 0) \\ \mathbf{c} &= c(0, 0, 1) \end{aligned} \quad (4)$$

and unit-cell positions (see Fig. 1):

$$\begin{aligned}
\mathbf{R}_1 &= \mathbf{0} \\
\mathbf{R}_2 &= u\mathbf{c} \\
\mathbf{R}_3 &= \frac{1}{3}\mathbf{a} + \frac{1}{3}\mathbf{b} + \frac{1}{2}\mathbf{c} \\
\mathbf{R}_4 &= \frac{1}{3}\mathbf{a} + \frac{1}{3}\mathbf{b} + \left(u + \frac{1}{2}\right)\mathbf{c}.
\end{aligned} \tag{5}$$

Under homogeneous strain, the lattice vectors and unit-cell positions transform as:

$$\mathbf{a}' = \hat{T}\mathbf{a}; \mathbf{b}' = \hat{T}\mathbf{b}; \mathbf{c}' = \hat{T}\mathbf{c} \tag{6a}$$

$$\begin{aligned}
\mathbf{R}'_1 &= \hat{T}\mathbf{R}_1 \\
\mathbf{R}'_2 &= \hat{T}\mathbf{R}_2 + \mathbf{t} \\
\mathbf{R}'_3 &= \hat{T}\mathbf{R}_3 + \mathbf{t}' \\
\mathbf{R}'_4 &= \hat{T}\mathbf{R}_4 + \mathbf{t} + \mathbf{t}',
\end{aligned} \tag{6b}$$

where $\hat{T} = \hat{1} + \hat{\varepsilon}$ and:

$$\hat{\varepsilon} = \begin{bmatrix} \varepsilon_{xx} & \varepsilon_{xy} & \varepsilon_{xz} \\ \varepsilon_{xy} & \varepsilon_{yy} & \varepsilon_{yz} \\ \varepsilon_{xz} & \varepsilon_{yz} & \varepsilon_{zz} \end{bmatrix} \tag{7}$$

is the strain tensor. $\mathbf{t} = (t_1, t_2, t_3)$ and $\mathbf{t}' = (t'_1, t'_2, t'_3)$ define rigid translations of the different sublattices (internal strains) that might be allowed by the reduced symmetry. We next introduce Eqs. (6) into Eq. (3), sum U_i over the four unit cell positions, expand the VFF energy to second order in ε_{ij} , t_i , and t'_i , then minimize the resulting expression with respect to the t_i and t'_i . We finally identify the VFF energy of the unit cell with the macroscopic elastic energy:

$$\begin{aligned}
E &= \Omega \left\{ \frac{1}{2}c_{11} (\varepsilon_{xx}^2 + \varepsilon_{yy}^2) + \frac{1}{2}c_{33}\varepsilon_{zz}^2 + c_{12}\varepsilon_{xx}\varepsilon_{yy} \right. \\
&\quad \left. + c_{13} (\varepsilon_{xx}\varepsilon_{zz} + \varepsilon_{yy}\varepsilon_{zz}) + 2c_{44} (\varepsilon_{yz}^2 + \varepsilon_{xz}^2) + 2c_{66}\varepsilon_{xy}^2 \right\}
\end{aligned} \tag{8}$$

where $\Omega = a^2 c \sqrt{3}/2$ is the volume of the unit cell. We get:

$$c_{11} = \frac{a^2}{2\sqrt{3}c} \frac{(4A^2 + 13AB + B^2)(8A'u^2 + 3B'w^2) + 162AB(A+B)v^2}{(2A+B)[8A'u^2 + 6(A+2B)v^2 + 3B'w^2]} \quad (9a)$$

$$c_{33} = \frac{3\sqrt{3}c^3}{4a^2} \frac{(A+2B)(8A'u^2v^2 + 3B'v^4) + 16A'B'u^4}{8A'u^2 + 6(A+2B)v^2 + 3B'w^2} \quad (9b)$$

$$c_{12} = \frac{a^2}{2\sqrt{3}c} \frac{(A-B)[(4A-B)(8A'u^2 + 3B'w^2) + 54ABv^2]}{(2A+B)[8A'u^2 + 6(A+2B)v^2 + 3B'w^2]} \quad (9c)$$

$$c_{13} = \frac{\sqrt{3}c}{2} \frac{(A-B)(8A'u^2 + 3B'vw)v}{8A'u^2 + 6(A+2B)v^2 + 3B'w^2} \quad (9d)$$

$$c_{44} = \frac{\sqrt{3}c}{4} \frac{(2A+B)B'}{(2A+B+B')} \quad (9e)$$

$$c_{66} = \frac{c_{11} - c_{12}}{2}, \quad (9f)$$

where $A = \alpha/r_0^2$, $A' = \alpha'/r_0'^2$, $B = \beta/r_0^2$, $B' = \beta'/(r_0r_0')$, and $w = 1 - 4u$. The internal translations which minimize the elastic energy moreover read:

$$\mathbf{t} = c(\zeta_1 \varepsilon_{xz}, \zeta_1 \varepsilon_{yz}, \zeta_2 (\varepsilon_{xx} + \varepsilon_{yy}) - \zeta_3 \varepsilon_{zz}) \quad (10a)$$

$$\mathbf{t}' = -a\zeta_4 \left(\varepsilon_{xy}, \frac{\varepsilon_{xx} - \varepsilon_{yy}}{2}, 0 \right), \quad (10b)$$

with internal strain parameters:

$$\zeta_1 = \frac{(2A+B)v - 2B'u}{2A+B+B'} \quad (11a)$$

$$\zeta_2 = \frac{2a^2}{c^2} \frac{(A-B)v}{8A'u^2 + 6(A+2B)v^2 + 3B'w^2} \quad (11b)$$

$$\zeta_3 = \frac{(8A'u^2 + 6B'vw)u - 3(A+2B)v^3}{8A'u^2 + 6(A+2B)v^2 + 3B'w^2} \quad (11c)$$

$$\zeta_4 = \frac{2}{\sqrt{3}} \frac{A-B}{2A+B}. \quad (11d)$$

Although we could have introduced two different sets of bond-bending constants for the anions and cations, only the average would have appeared in the above expressions. In the ideal wurtzite ($c = a\sqrt{8/3}$, $u = 3/8$, $\alpha = \alpha'$ and $\beta = \beta'$),

Eqs. (9) reduce to [19, 20, 22]:

$$c_{11} = \frac{1}{4\sqrt{3}r_0} \frac{6\alpha^3 + \beta^3 + 37\alpha^2\beta + 28\alpha\beta^2}{(\alpha + \beta)(2\alpha + \beta)} \quad (12a)$$

$$c_{33} = \frac{1}{4\sqrt{3}r_0} \frac{3\alpha^2 + \beta^2 + 20\alpha\beta}{\alpha + \beta} \quad (12b)$$

$$c_{12} = \frac{1}{4\sqrt{3}r_0} \frac{\alpha - \beta}{\alpha + \beta} \frac{6\alpha^2 - \beta^2 + 7\alpha\beta}{2\alpha + \beta} \quad (12c)$$

$$c_{13} = \frac{1}{4\sqrt{3}r_0} \frac{\alpha - \beta}{\alpha + \beta} (3\alpha - \beta) \quad (12d)$$

$$c_{44} = \frac{1}{\sqrt{3}r_0} \beta \frac{2\alpha + \beta}{\alpha + \beta}, \quad (12e)$$

where $r_0 = r'_0$ is the equilibrium bond length.

Finally, we would like to emphasize that this model provides a *local* description of the elasticity of wurtzite materials similar to continuum elasticity theory. It misses, in particular, the long range electro-mechanical couplings due to pyro- and piezo-electricity. Although these couplings are actually often neglected (“semi-coupled” approach), they can be significant in some III-V devices [24, 25]. If needed, electro-mechanical couplings might be taken into account in this model by introducing transverse or piezo-electric charges on the atoms which couple to the macroscopic pyro- and piezo-electric fields [23].

3. Application to GaN, AlN and InN

As an illustration, we have computed bond-stretching and bond-bending constants for wurtzite GaN, AlN and InN (see Table 1). They were fitted to the macroscopic elastic constants of Ref. [21]. We have assumed $\alpha = \alpha'$ and $\beta = \beta'$, which already gives a good account of the elastic properties of these materials (marginal improvement was obtained with $\alpha \neq \alpha'$ and $\beta \neq \beta'$).

The VFF elastic constants c_{ij} , bulk modulus

$$B = \frac{c_{33}(c_{11} + c_{12}) - 2c_{13}^2}{c_{11} + c_{12} + 2c_{33} - 4c_{13}} \quad (13)$$

and the ratio

$$R = \frac{\varepsilon_{\perp}}{\varepsilon_{\parallel}} = 2 \frac{c_{13}}{c_{33}} \quad (14)$$

	GaN	AlN	InN	
a	3.189	3.112	3.544	Å
c	5.185	4.982	5.718	Å
u	0.3768	0.3819	0.3790	
α	88.35	83.79	67.38	N/m
β	20.92	19.83	10.01	N/m
c_{11}	389.9 (390.0)	391.6 (396.0)	226.6 (223.0)	GPa
c_{33}	404.9 (398.0)	373.6 (373.0)	223.4 (224.0)	GPa
c_{12}	138.9 (145.0)	141.1 (137.0)	112.6 (115.0)	GPa
c_{13}	110.6 (106.0)	105.4 (108.0)	93.3 (92.0)	GPa
c_{44}	111.6 (105.0)	107.6 (116.0)	49.5 (48.0)	GPa
B	211.6 (210.0)	206.0 (207.2)	141.4 (140.6)	GPa
R	0.547 (0.533)	0.564 (0.579)	0.835 (0.821)	
ζ_2	0.08 (0.09)	0.08 (0.09)	0.09	
ζ_3	0.16 (0.17)	0.17 (0.19)	0.20	

Table 1: Lattice parameters, bond-stretching and bond-bending constants of wurtzite GaN and AlN. The elastic constants c_{ij} computed from Eq. (9) are given and compared to the experimental or *ab initio* data (in parenthesis) [21].

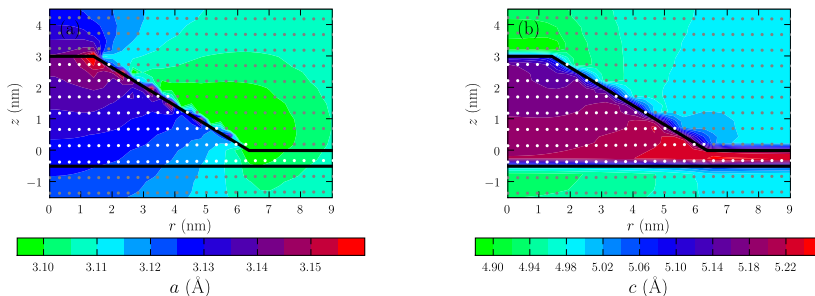


Figure 2: (Color online) Local lattice parameters a (a) and c (b) computed with Keating's VFF in a GaN/AlN quantum dot. They were computed from the spacings between atomic rows and columns belonging to the same cation sublattice, and are plotted in a **(a, c)** plane containing the axis of the dot. The white and gray dots are Ga and Al atoms respectively.

of the perpendicular to parallel biaxial [0001] strain are compared with the data of Ref. [21] in Table 1. The internal strain parameters ζ_2 and ζ_3 of GaN and AlN are also compared with the *ab initio* values deduced from Ref. [26]. The c_{ij} 's are within 5% of Ref. [21] (within the experimental error bars), with the exception of c_{44} , which is $\simeq 7\%$ wrong in GaN and AlN. The bulk moduli are within 1% of the experimental values, and R within 2.5%. The internal strain parameters are also fairly well reproduced. This two parameters VFF model is therefore able to describe the elasticity of GaN, AlN and InN in a very satisfactory way.

As a test and example of application, we have computed the strains in a GaN/AlN quantum dot similar to Fig. 4 of Ref. [27]. The GaN dot is modeled as a truncated cone with base and top diameters of 13.3 and 3 nm respectively and a height of 3 nm. It lies on a 5 Å thick wetting layer. The dot is embedded in AlN and periodic boundary conditions are applied on a $(40 \text{ nm})^3$ box. The atomic positions are relaxed with a conjugate gradients algorithm [28]. The local lattice parameters a and c are plotted in Fig. 2 in a **(a, c)** plane containing the axis of the dot. They were computed from the spacings between atomic rows and columns belonging to the same cation sublattice. They are quite similar to those of Ref. [27], computed with continuum elasticity theory and Eshelby's inclusion method. They show, however, much smoother variations around the interfaces than continuum elasticity theory, because a and c are only defined on

the scale of an unit cell. This VFF model was also used in Ref. [29] to study GaN insertions in AlN nanocolumns.

4. Conclusion

We have discussed the application of Keating's valence force field model to non-ideal wurtzite materials. We have derived, in particular, the relations between the macroscopic elastic constants c_{ij} and the microscopic bond-stretching and bond-bending constants α and β for arbitrary c/a and u . This model gives a satisfactory description of the elasticity of nitride materials (GaN, AlN and InN). It directly provides atomic positions suitable, for example, for atomistic electronic structure methods.

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