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Operator ordering, ellipticity and spurious solutions in $\mathbf{k}\cdot\mathbf{p}$ calculations of III-nitride nanostructures

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Abstract We analyze the ellipticity of the standard $\mathbf{k}\cdot\mathbf{p}$ wurtzite model for the symmetrized and the Burt–Foreman operator ordering. We find that for certain situations the symmetrized Hamiltonian is unstable, leads to unplausible results and can cause spurious solutions. We show that the operator ordering in wurtzite must be completely asymmetric to be stable. The asymmetric operator ordering is elliptic and consequently no spurious solutions are obtained. Therefore we recommend the use of a complete asymmetric operator ordering for nitride device simulation.

Keywords $\mathbf{k}\cdot\mathbf{p}$ · Spurious solutions · Finite element method · Nanostructures · Operator ordering · Nitride · Wurtzite

1 Introduction

In the numerical modeling of optoelectronic devices, the electronic properties of the active regions are often determined using the $\mathbf{k}\cdot\mathbf{p}$ envelope function theory (EFT). Its formulation as a coupled system of partial differential equations requires only a modest computational effort. Therefore systems of quantum wells, wires or dots can be solved on standard workstations using plane-wave expansions, finite differences or finite elements. An important issue (in the EFT) is the correct ordering of the differential operators. Starting from bulk $\mathbf{k}\cdot\mathbf{p}$ terms, one replaces the wavenumbers k_j by operators $-i\,\partial_j$. As an example, second order terms are transformed according to

$$\widetilde{\mathbf{H}}^{(2)}_{ij} k_i k_j \rightarrow -\partial_i \mathbf{H}^{(2)}_{ij} \partial_j - \partial_j \mathbf{H}^{(2)}_{ji} \partial_i . \tag{1}$$

Here, $\widetilde{\mathbf{H}}^{(2)}_{ij}$ represents the coefficient matrix of the terms proportional to $k_i k_j$ in the designated $\mathbf{k}\cdot\mathbf{p}$ matrix. In a bulk crystal, the wavenumber operator commutes with the coefficients

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and therefore, the information of the splitting of $\widetilde{\mathbf{H}}_{ij}^{(2)}$ into $\mathbf{H}_{ij}^{(2)}$ and $\mathbf{H}_{ji}^{(2)}$ is lost. Due to lack of knowledge, usual implementations use a symmetric distribution to obtain a hermitian equation system. Burt (1992, 1999) discovered that the operator ordering could be derived from the heterostructure's Schrodinger equation. He concluded that, the operator ordering is hermitian, but not necessarily symmetric. Foreman (1997) then derived the operator ordering for zinc-blende models, which is referred to as the Burt–Foreman (BF) ordering.

With the advent of blue- and green-light emitting diodes, modeling of nitride nanostructures with wurtzite crystal symmetry attracts much attention. Usual calculations are based on the symmetrized version of the wurtzite Hamiltonian (Chuang and Chung 1996). Mireless and Ulloa (1999) derived the corresponding operator ordering and demonstrated the underestimation of the coupling to remote d-like states in the symmetrized version of the Hamiltonian. The derivation of the operator ordering given by Ram-Mohan and Yoo (2006) differs slightly from Mireless and Ulloa (1999), as their analysis employs one additional parameter, leading to parameters which can only be determined from first principle calculations.

In this work, we analyze the 6×6 $\mathbf{k}\cdot\mathbf{p}$ Hamiltonian of Chuang and Chung (1996) and show that the symmetrized Hamiltonian is unstable and leads to spurious solutions. We then use the ellipticity analysis (as presented in Veprek et al. (2007) for zinc-blende materials) to suggest a stable operator ordering.

2 Effect of operator ordering on wurtzite quantum wells and quantum wires

In the $\mathbf{k}\cdot\mathbf{p}$ theory, the Löwdin perturbation technique (Löwdin 1951) is usually used to reduce the Hamiltonian to a smaller number of relevant bands, including the effect of the reduced bands perturbatively. Using the notation of Stavrinou and Dalen (1997), the Löwdin interaction term on the remaining bands is given by

$$H_{jj'}^{int} = \frac{\hbar^2}{m_0^2} \sum_{\alpha,\beta=x,y,z} \hat{k}_\alpha \left(\sum_\nu \frac{\langle j|\hat{p}_\alpha|\nu\rangle\langle\nu|\hat{p}_\beta|j'\rangle}{E - E_\nu} \right) \hat{k}_\beta . \tag{2}$$

Here, the sum runs over all reduced remote bands ν. In a heterostructure with material dependent matrix elements, the operators $\hat{k}_\cdot$ do not commute with the position dependent coefficients and therefore, have to remain in their correct order. The Hamiltonian of Chuang and Chung (1996) including the operator ordering is given by[1]

$$\begin{pmatrix} F+\varrho & \kappa^* & \xi & 0 & 0 & 0 \\ \kappa & G-\varrho & -\xi^* & 0 & 0 & \Delta \\ \eta^* & -\eta & \lambda & 0 & \Delta & 0 \\ 0 & 0 & 0 & F-\varrho & \kappa & -\xi^* \\ 0 & 0 & \Delta & \kappa^* & G+\varrho & \xi \\ 0 & \Delta & 0 & -\eta & \eta^* & \lambda \end{pmatrix}, \tag{3}$$

where

[1] For the bulk crystal, the matrix (3) is identical to the transpose of Chuang and Chung (1996). It follows the derivation presented in Bir and Pikus (1974).

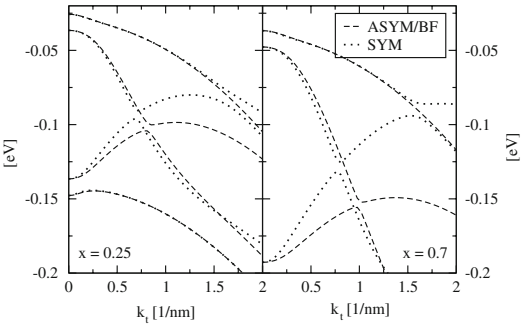

Fig. 1 In-plane dispersion of a 1.5 nm GaN—$Al_{0.25}Ga_{0.75}N$ (left) and GaN—$Al_{0.7}Ga_{0.3}N$ (right) quantum well. The dashed line denote results obtained with asymmetric (Burt–Foreman) ordering while the dotted dispersions were obtained using the symmetrized Hamiltonian

$$
\begin{aligned}
&F = \Delta_1 + \Delta_2 + \lambda + \theta \qquad G = \Delta_1 - \Delta_2 + \lambda + \theta \\
&\lambda = \hat{k}_z A_1 \hat{k}_z + \hat{k}_x A_2 \hat{k}_x + \hat{k}_y A_2 \hat{k}_y \qquad \theta = \hat{k}_z A_3 \hat{k}_z + \hat{k}_x A_4 \hat{k}_x + \hat{k}_y A_4 \hat{k}_y \\
&\kappa = -\hat{k}_x A_5 \hat{k}_x + \hat{k}_y A_5 \hat{k}_y + i(\hat{k}_x A_5 \hat{k}_y + \hat{k}_y A_5 \hat{k}_x) \qquad (4) \\
&\eta = -\hat{k}_z A_6^+ (\hat{k}_x + i\hat{k}_y) - (\hat{k}_x + i\hat{k}_y) A_6^- \hat{k}_z \qquad \xi = -\hat{k}_z A_6^- (\hat{k}_x + i\hat{k}_y) - (\hat{k}_x + i\hat{k}_y) A_6^+ \hat{k}_z \\
&\varrho = i\hat{k}_y (A_5^+ - A_5^-)\hat{k}_x - i\hat{k}_x (A_5^+ - A_5^-)\hat{k}_y \qquad \Delta = \sqrt{2}\Delta_3.
\end{aligned}
$$

The parameters A_5 and A_6 are split into two asymmetric parts

$$A_i = A_i^+ + A_i^- . \qquad (5)$$

In (3), the effect of k-dependent spin orbit splitting (via the A_7 parameter, Bir and Pikus 1974; Ren et al. 1999) and the strain dependence have been neglected. In a bulk crystal, (3) reduces into the usual form. The heterostructure Hamiltonian (3) has a more complicated form on the off-diagonal terms κ, η and ξ, and also includes a term ϱ on the diagonal which cancels in bulk.

In Mireless and Ulloa (1999), it was shown that BF operator ordering does lead to significantly different results when the parameters of the involved materials change by a significant amount at the heterointerface. This is illustrated in Fig. 1 where the difference in the band structure of a 1.5 nm wide GaN quantum well embedded in AlGaN is plotted. The material parameters are taken from Vurgaftman and Meyer (2003) for all calculations. The results were obtained using the finite element $\mathbf{k} \cdot \mathbf{p}$ solver *tdkp* (Veprek et al. 2008). The left and right figure correspond to Al molefractions (mf) of 0.25 and 0.7. The dashed line denotes the calculation using a completely asymmetric ordering while the dotted line denotes the results obtained with the symmetrized Hamiltonian. The difference is significant and increases with increasing Al content (and therefore, increasing parameter difference between barrier and well material). Increasing the Al content further would lead to subbands bending into the forbidden band gap for the symmetric ordering. If similar calculations are performed for a square 1.8 nm^2 quantum wire using the same material system, the effects are even more dramatic, as can be seen from Fig. 2. For the material system with an Al mf of 0.25, the symmetrized Hamiltonian leads to stronger confined states and dispersions differing by more than 25 meV. In the calculation with an Al mf of 0.7, symmetrized operator ordering yields spurious states above the upper valence band-edge of GaN (which is at 0.0156 eV). In Fig. 3, the probability density of the top valence band state in the quantum wire is plotted for both orderings. The state corresponding to symmetric operator ordering is spuriously localized at the corners of the structure. The results obtained using BF operator ordering are still in a reasonable form and not affected by any spurious solution. These findings can be explained in terms of the ellipticity of the given equation system.

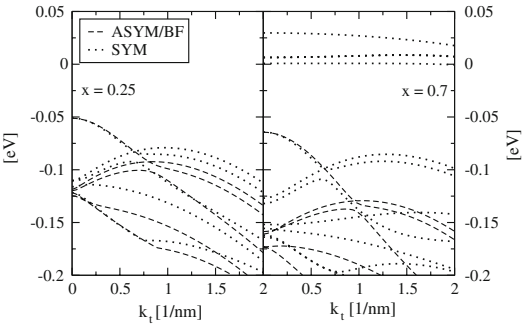

Fig. 2 Dispersion of a fictive 1.8 nm^2 square GaN—$Al_{0.25}Ga_{0.75}N$ (left) and GaN—$Al_{0.7}Ga_{0.3}N$ (right) quantum wire, calculated with BF and symmetric operator ordering

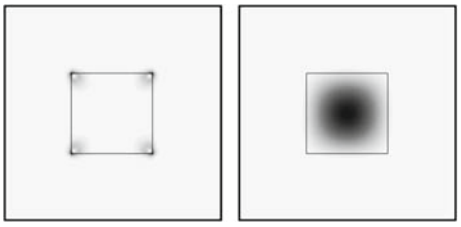

Fig. 3 Probability distribution of top valence band state in a fictive 1.8 nm^2 square GaN—$Al_{0.7}Ga_{0.3}N$ quantum wire, calculated with symmetric (left) and BF operator ordering (right). The symmetric ordering leads to a state spuriously localized at the corners of the structure

3 Ellipticity analysis of wurtzite $\mathbf{k}\cdot\mathbf{p}$ model

The bilinear form of the coupled equation system given by the EFT is in analogy to a scalar second order partial differential operator given by (Veprek et al. 2007)

$$\hat{\alpha}(\mathbf{f},\mathbf{v}) = \int_{\Omega} \sum_{ijkl} \partial_i v_k^{\star}\, h_{ij}^{kl}\, \partial_j f_l, \tag{6}$$

where $h_{ij}^{kl} \equiv (\mathbf{H}_{ij}^{(2)})_{kl}$. Here, k, l run over the Bloch-band indices $[1, m]$ depending on the number of Bloch-bands involved. i, j run over the directions of the system. The bilinear form of an elliptic equation is convex. This is fulfilled if the coefficient matrix h_{ij}^{kl} is definite. If h_{ij}^{kl} has both eigenvalues with positive and negative signs, the equation system is non-elliptic. As outlined in Veprek et al. (2007), the lack of ellipticity of the designated equations changes their mathematical nature, leading to an improperly-posed problem. Solutions of these equations then depend on the applied discretization method and may appear as being spurious. The second order terms of the $\mathbf{k}\cdot\mathbf{p}$ 6×6 matrix decouple into two similar 3×3 blocks, hence only one block must be analyzed. The associated matrix h_{ij}^{kl} is given by

$$\begin{pmatrix}
A_2+A_4 & -A_5 & 0 & i(A_5^- - A_5^+) & -i(A_5^- + A_5^+) & 0 & 0 & 0 & -A_6^+ \\
-A_5 & A_2+A_4 & 0 & i(A_5^- + A_5^+) & -i(A_5^- - A_5^+) & 0 & 0 & 0 & A_6^+ \\
0 & 0 & A_2 & 0 & 0 & 0 & -A_6^- & A_6^- & 0 \\
-i(A_5^- - A_5^+) & -i(A_5^- + A_5^+) & 0 & A_2+A_4 & A_5 & 0 & 0 & 0 & -iA_6^+ \\
i(A_5^- + A_5^+) & i(A_5^- - A_5^+) & 0 & A_5 & A_2+A_4 & 0 & 0 & 0 & -iA_6^+ \\
0 & 0 & 0 & 0 & 0 & A_2 & iA_6^- & iA_6^- & 0 \\
0 & 0 & -A_6^- & 0 & 0 & -iA_6^- & A_1+A_3 & 0 & 0 \\
0 & 0 & A_6^- & 0 & 0 & -iA_6^- & 0 & A_1+A_3 & 0 \\
-A_6^+ & A_6^+ & 0 & iA_6^+ & iA_6^+ & 0 & 0 & 0 & A_1
\end{pmatrix}. \tag{7}$$

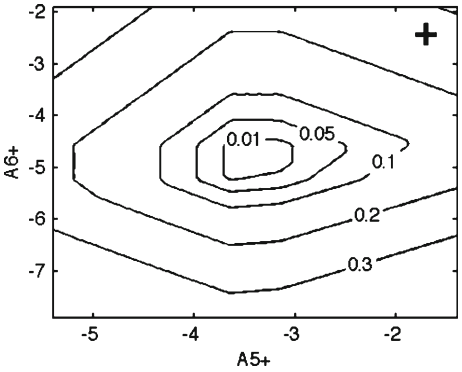

Fig. 4 Degree of non-ellipticity (8) for different choice of the splitting for parameters A_{i+} and A_{i-} in GaN ($A_5 = -3.4$, $A_6 = -4.9$ and other parameters were taken from Vurgaftman and Meyer (2003)). The equations are elliptic for $\rho = 0$. The cross denotes the symmetric splitting

To quantify the non-ellipticity of a given parameter set, one defines the ratio between positive and negative eigenvalues λ_i of h_{ij}^{kl} by (Veprek et al. 2007)

$$\rho = \left| \frac{\sum_{i,\lambda_i>0} \lambda_i}{\sum_{j,\lambda_j<0} \lambda_j} \right|. \tag{8}$$

In order to determine the optimal splitting, we calculate eigenvalues of the second order coefficient matrix h_{ij}^{kl} for different choices of $A_{5,+}$ and $A_{6,+}$ and plot the non-ellipticity ratio (8) for each combination. In Fig. 4, the situation for GaN parameters is shown.

The equation is elliptic only for a completely asymmetric distribution between $A_{i,+}$ and $A_{i,-}$ for both parameters A_5 and A_6. Any significant deviation from the completely asymmetric splitting leads to increasing non-ellipticity. The non-ellipticity of the symmetrized operator ordering is indicated with the cross in Fig. 4. Obviously, the symmetrized operator ordering is highly non-elliptic. For AlN and InN, we obtain very similar results. These materials also require a complete asymmetric split between $A_{i,+}$ and $A_{i,-}$. The complete asymmetric split is not only required for the effective mass parameters A_i of Vurgaftman and Meyer (2003), but also for the parameters given by Ren et al. (1999); Dugdale et al. (2000); Kim et al. (1997), and Rezaei et al. (2006).

4 Conclusion

The symmetrized wurtzite $\mathbf{k} \cdot \mathbf{p}$ Hamiltonian of Chuang and Chung (1996) is numerically unstable for material systems with a significant discontinuity of the material parameters at interfaces. Its application to quantum wires can lead to spurious solutions, depending on the involved materials. The associated problems are caused by the lack of ellipticity due to wrong operator ordering, as it was already found for zinc-blende $\mathbf{k} \cdot \mathbf{p}$ models (Veprek et al. 2007). The suggested complete asymmetric operator ordering reestablishes the ellipticity of the equation system and leads to stable and spurious solution free band structures. The ordering has also been motivated physically in Mireless and Ulloa (1999), although their estimate suggests a less asymmetric distribution. As the asymmetric operator ordering leads to reliable band structures in nanostructures of all dimensions and for all material systems, it is recommended for nitride device simulation.

References

Bir, G.L., Pikus, G.E.: Symmetry and strain-induced effects in semiconductors. Wiley, New York (1974)

Burt, M.G.: The justification for applying the effective-mass approximation to microstructures. J. Phys. Condens. Matter. **4**, 6651–6690 (1992)

Burt, M.G.: Fundamentals of envelope function theory for electronic states and photonic modes in nanostructures. J.Phys. Condens. Matter. **11**, R53–R83 (1999)

Chuang, S.L., Chang, C.S.: $\mathbf{k}\cdot\mathbf{p}$ method for strained wurtzite semiconductors. Phys. Rev. B. **54**, 2491 (1996)

Dugdale, D.J., Brand, S., Abram, R.A.: Direct calculation of $\mathbf{k}\cdot\mathbf{p}$ parameters for wurtzite AlN, GaN, and InN. Phys. Rev. B. **61**, 12933 (2000)

Foreman, B.A.: Elimination of spurious solutions from eight-band $\mathbf{k}\cdot\mathbf{p}$ theory. Phys. Rev. B. **56**, R12748 (1997)

Kim, K., Lambrecht, W.R.L., Segall, B.: Effective masses and valence-band splittings in GaN and AlN. Phys. Rev. B. **56**, 7363 (1997)

Löwdin, P.: A note on the quantum-mechanical perturbation theory. J. Chem. Phys. **19**, 1396–1401 (1951)

Mireles, F., Ulloa, S.E.: Ordered hamiltonian and matching conditions for heterojunctions with wurtzite symmetry: GaN/$Al_xGa_{1-x}N$ quantum wells. Phys. Rev. B. **60**, 13659 (1999)

Ram-Mohan, L.R., Yoo, K.H.: Wavefunction engineering of layered semiconductors: theoretical foundations. J. Phys. Condens. Matter. **18**, R901–R917 (2006)

Ren, G.B., Liu, Y.M., Blood, P.: Valence-band structure of wurtzite GaN including the spin-orbit interaction. Appl. Phys. Lett. **74**, 1117–1119 (1999)

Rezaei, B., Asgari, A., Kalafi, M.: Electronic band structure pseudopotential calculation of wurtzite III-nitride materials. Physica B. **371**, 107 (2006)

Stavrinou, P.N., van Dalen, R.: Operator ordering and boundary conditions for valence-band modeling: application to [110] heterostructures. Phys. Rev. B. **55**, 15456–15459 (1997)

Veprek, R.G., Steiger, S., Witzigmann, B.: Ellipticity and the spurious solution problem of $\mathbf{k}\cdot\mathbf{p}$ envelope equations. Phys. Rev. B. **76**, 165320 (2007)

Veprek, R.G., Steiger, S., Witzigmann, B.: J. Comp. El. **7**, 521–529 (2008)

Vurgaftman, I., Meyer, J.R.: Band parameters for nitrogen-containing semiconductors. Appl. Phys. Rev. **94**, 3675 (2003)