System-Dependent Modified Becke-Johnson Exchange for Quantum Transport Simulations

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Introduction To achieve broader versatility and better prediction quality the framework of quantum transport simulations gradually evolves from the tight-binding method towards the Density Functional Theory (DFT). The two major obstacles for this evolution are the high computational cost of the DFT and its inability to reproduce the correct band gaps for most of the materials. The modified Becke-Johnson (m-BJ) exchange functional recently suggested by Blaha and Tran (BT) allows for a substantial improvement both in terms of computational efficiency and band gap precision [1], [2]. These improvements were demonstrated on a wide range of materials using augmented plane-wave full-core calculations. However, neither plane-wave nor all-electron approaches are well suited for simulation of electron current through nano-scale devices. A large problem size makes imperative the use of pseudopotentials and localized orbitals are required to account for non-periodic nature of the device.

As part of a broader effort in developing Gaussian-based DFT electron transport code, we have selected 15 technologically important semiconductors, namely AlAs, Bi_2Te_3, GaAs, GaN, GaP, GaSb, Ge, HfO_2, InAs, InP, InSb, PbTe, ScN, Si, and SiC to adjust parameterization of m-BJ exchange functional for use with Bachelet, Hamann, and Schlüter pseudopotentials (BHS-PP) [3]. Such adjustment is necessary because (*i*) pseudo- and all-electron wave functions differ in the vicinity of nuclei and hence lead to different exchange potentials, and (*ii*) pseudopotentials are designed for use with specific exchange-correlation functional, i.e. the use of m-BJ exchange together with BHS-PP derived in the local density approximation (LDA) may incur substantial errors.

Parameterization Strategy The functional form of m-BJ BT exchange potential is as follows:

$$v_x^{mBJ}(\mathbf{r}) = v_x^{BR}(\mathbf{r}) + \frac{3c-2}{\pi}\sqrt{\frac{5t(\mathbf{r})}{6\rho(\mathbf{r})}} \quad (1)$$

Here $t(\mathbf{r}) = \sum_{i=1}^{N} |\nabla\psi_i(\mathbf{r})|^2$ is the kinetic energy, ψ_i is the ith Kohn-Sham orbital, v_x^{BR} the Becke-Roussel exchange [4], and $\rho(\mathbf{r})$ the electron density. The key parameter c allows for band gap tuning: an increase of c leads to a monotonous increase of the band gap from an underestimated LDA value to an overestimated exact exchange. Hence, it is guaranteed that there exists a value of $c = c_{ex}$ reproducing the experimental band gap energy even if LDA predicts zero band gap as for InSb (Fig. 1) or InAs (Fig. 2). The value of c_{ex} is material specific and therefore a functional of electron density. Blaha and Tran suggested that $c = A + B\,\langle g\rangle$, where $\langle g\rangle$ is the normalized electron density gradient averaged over the unit cell volume V_{uc}:

$$\langle g\rangle = V_{uc}^{-1}\int_{V_{uc}} |\nabla\rho(\mathbf{r})|/\rho(\mathbf{r})\; d\mathbf{r} \quad , \quad (2)$$

with the universal constants A and B chosen to best fit the experimental band gap of a large material set.

Leaving intact Eq.(1) we allow for other physical quantities averaged similarly to $\langle g\rangle$ to participate in a search of the parameterization functional form for c. Let Ω designate the set of such averaged parameters. Each element of Ω is a one-to-one function of c, which means that variation of c corresponds to some material-specific curve in the space with dimension of Ω. Such curve can be viewed as a function of parametric variable x, i.e. scalar c depends on scalar x, while x depends on Ω. If there are no restrictions on the functional form of x, then, without a loss of generality, a linear dependence of c over x can be assumed: $c = A + B\;x\,(\Omega)$, where the constants A, B and function x are chosen from the best fit to the experimental band gaps.

Discussion Indeed, a combination of BHS-PP and the original BT parameterization leads to a poor band gap fit. Nevertheless the m-BJ framework can yield much better fits in conjunction with BHS-PP if the suggested alternative parameterizations of c are used. Such parameterizations can embrace either the full set of 15 semiconductors considered here or smaller subsets. For example, the parameterization depicted in Fig. 3 for a set of eight III-V materials and crystalline hafnium dioxide (AlAs, GaAs, GaN, GaP, GaSb, InAs, InP, InSb, HfO_2) results in a Mean Absolute value of the Relative band gap Error (MARE_{Eg}) of less than 4%. If one intends to model SiGe transistors doped with arsenic and phosphorus and with hafnium dioxide serving as a gate insulator, a set containing Si, Ge, HfO_2, AlAs, GaAs, GaP may be chosen for parameters generation. As shown in Fig. 4 the MARE_{Eg} for this subset equals only 1%.

Parameterizations are based on precomputed derivatives $dc/dx|_{x=x_{ex}}$ depicted as line segments tangential to curves $c_{ex,i}(x)$ passing through c_{ex} for material i. These tangents are used to project the intersection point between $A\,x + B$ and $c_{ex,i}(x)$ and to evaluate band gap errors from the precomputed derivatives $dE_{g,i}/dc|_{c=c_{ex,i}}$. That makes the parameterization process numerically efficient and allows for an *on the fly* parameter generation for each specific device.

Figure 5 reports c_{ex} for all the 15 materials considered here with MARE_{Eg} = 12.5%. Given that BT parameterization comprises 40 materials and has MARE_{Eg} = 10.5%, we conclude that the BT parameterization within the full core model has a higher predictive quality. However, even MARE_{Eg} = 10.5% would be too high for many transport problems, which calls for the device-specific parameterizations like those in Figs. 3 and 4.

Conclusion A substantial incompatibility between the original m-BJ parameterization and BHS-PP framework has been observed. The alternative parameterizations of the variable c based on first-order error predictions leads to reasonable band gap fits with relative band gap errors for device-specific parameterizations within few percent.

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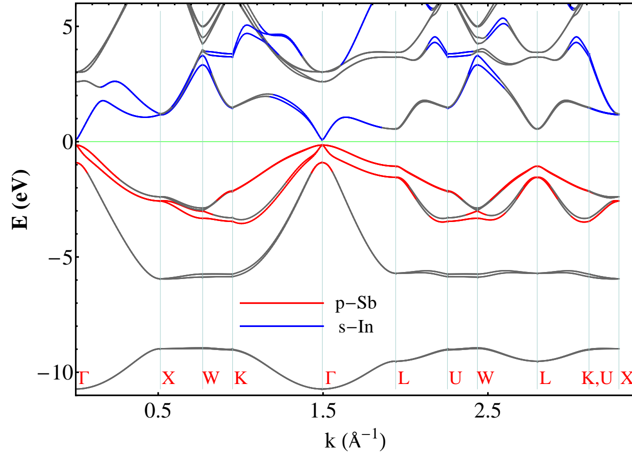

Fig. 1. m-BJ band structure of InSb. The experimental value of the T = 0 K band gap $E_g = 0.238$ eV is achieved for $c = 0.934$. Colors are used to indicate the predominant contribution of the specific orbital types.

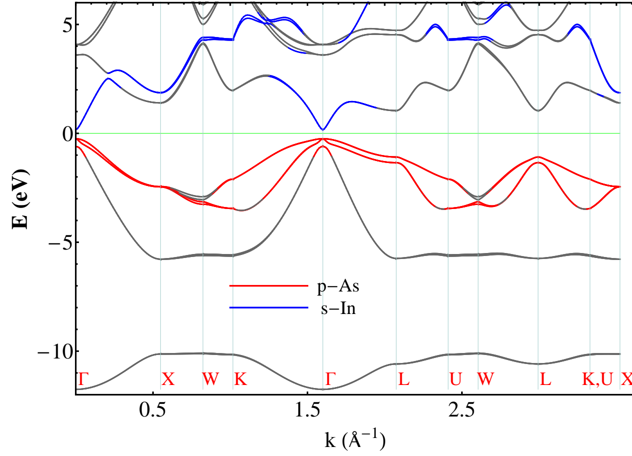

Fig. 2. m-BJ band structure of InAs. The experimental value of the T = 0 K band gap $E_g = 0.419$ eV is achieved for $c = 0.888$. Colors are used to indicate the predominant contribution of the specific orbital types.

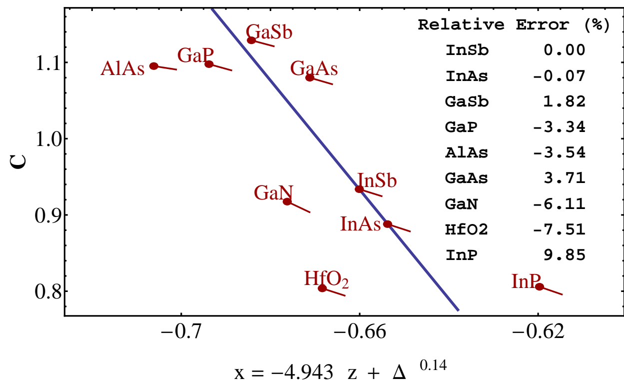

Fig. 3. Set $\Omega = \{\langle\Delta\rangle, \langle z\rangle\}$. Here $z(\mathbf{r}) = \frac{t(\mathbf{r})}{t_W(\mathbf{r})}$ is the inhomogeneity parameter, $t_W(\mathbf{r}) = \frac{|\nabla\rho(\mathbf{r})|^2}{8\rho(\mathbf{r})}$ the Weizsäcker kinetic-energy density, $\Delta(\mathbf{r}) = \nabla^2\rho(\mathbf{r}) \Big/ \left(4\left(3\pi^2\right)^{2/3}\rho(\mathbf{r})^{5/3}\right)$ the reduced Laplacian of the electron density. Function $c(x) = -7.158\ x\left(\langle z\rangle, \langle\Delta\rangle\right) - 3.791$ was optimized with 4-parameter fit for a set of 9 materials yielding MARE$_{Eg}$ = 4.0%.

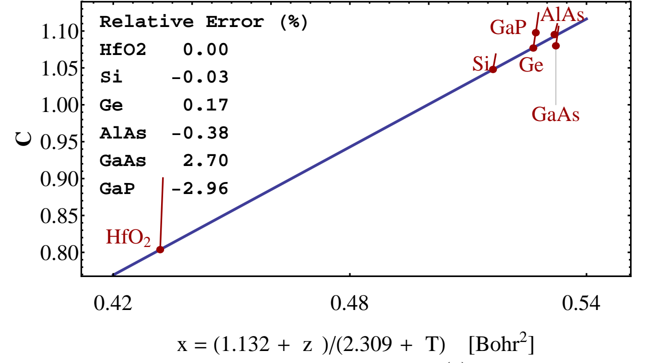

Fig. 4. Set $\Omega = \{\langle T\rangle, \langle z\rangle\}$. Here $T(\mathbf{r}) = \frac{t(\mathbf{r})}{\rho(\mathbf{r})}$ is the normalized kinetic energy density, $z(\mathbf{r}) = \frac{t(\mathbf{r})}{t_W(\mathbf{r})}$ the inhomogeneity parameter and $t_W(\mathbf{r}) = \frac{|\nabla\rho(\mathbf{r})|^2}{8\rho(\mathbf{r})}$ the Weizsäcker kinetic-energy density. Function $c(x) = 2.892\ x\left(\langle T\rangle, \langle z\rangle\right) - 0.446$ was optimized with 4-parameter fit for a set of 6 materials. MARE$_{Eg}$ = 1.0%.

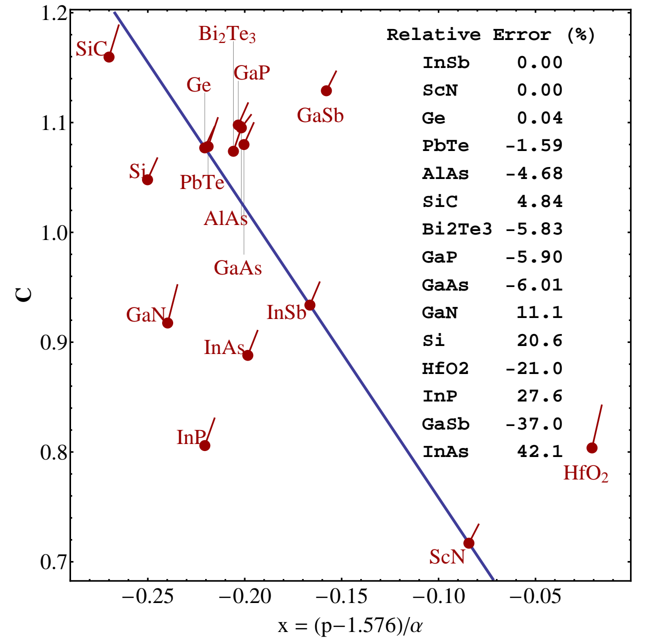

Fig. 5. Set $\Omega = \{\langle p\rangle, \langle\alpha\rangle\}$. Here $\alpha(\mathbf{r}) = \frac{t(\mathbf{r}) - t_W(\mathbf{r})}{t_{TF}(\mathbf{r})}$ is the deviation from the Weizsäcker kinetic-energy density normalized to the Tomas-Fermi kinetic energy density $t_{TF}(\mathbf{r}) = (3/10)\left(3\pi\right)^{2/3}\rho(\mathbf{r})^{5/3}$ and $p(\mathbf{r}) = |\nabla\rho(\mathbf{r})|^2 \Big/ \left(4\left(3\pi^2\right)^{2/3}\rho(\mathbf{r})^{8/3}\right)$ is the inhomogeneity parameter. Function $c(x) = -2.643\ x\left(\langle p\rangle, \langle\alpha\rangle\right) + 0.494$ was optimized with 3-parameter fit for a set of 15 materials. MARE$_{Eg}$ = 12.5%.

References

[1] F. Tran and P. Blaha, Physical Review Letters **102**, 226401 (2009).
[2] D. Koller, F. Tran and P. Blaha, Physical Review B **85**, 155109 (2012).
[3] G. B. Bachelet, D. R. Hamann, and M. Schlüter, Physical Review B **26**, 4199 (1982).
[4] A. D. Becke and M. R. Roussel, Physical Review A **39**, 3761 (1989).