Empirical tight-binding parameterizations for accurate heterostructure and alloy calculations

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***Abstract*—Empirical tight-binding is a valuable and reliable tool for the calculation of electronic and optical properties in semiconductor heterostructures and alloys. It has been applied in many contexts, ranging from inorganic semiconductors like arsenides, antimonides, nitrides and their alloys to 2D materials and hybrid perovskites. Here we present recent activities in development and application of empirical tight-binding, in particular regarding disordered alloys. We show some limitations of the most used schemes, and how they can be overcome by more recent parameterizations, and we introduce an alternative machine-learning based parameterization scheme.**

***Index Terms*—empirical tight-binding, alloys, parameterization, machin-learning**

I. Introduction

Empirical tight-binding (ETB) has proven to be extremely useful for the simulation of optoelectronic devices, when details of the atomistic structure matter, but ab-initio approaches like DFT are not feasible. ETB has been used in the last decades in particular for studying random alloy and disorder effects in III-nitrides, like InGaN quantum-well structures, and for III-V based alloys [1, 2].

A popular ETB parameterization for III-Vs and III-nitrides is due to Jancu and co-workers [3]. It uses an orthogonal, nearest-neighbor $sp^3d^5s^*$ parameterization, with Harrison scaling for the bond-length dependence of the hopping parameters, and the onsite parameters for common atoms inside of material families are nearly consistent. We regard this latter property as important, as it relates to the transferability of the parameters and therefore their applicability in alloy and heterostructure calculations.

A common feature of ETB models is that the empirical parameters are usually found by fitting the ETB bandstructure obtained for pure bulk materials to DFT data. Depending on how this is done exactly can lead to ambiguities when transferring the parameters to alloys and heterostructure. We recently found, that the parameterization from Ref. [3] well reproduce alloy band gaps and bowing for group-III alloying, but less so for group-V alloying [4]. One of the major reasons for this seems to be that in the most prominent ETB schemes the local Hamiltonian depends on the local atomic environment only via the hopping matrix elements (both due to the atom types and due to bond length scaling), while onsite matrix elements are fixed. However, it can be expected that variations in the atomic environment from the pure bulk material induces modifications both in onsite and hopping matrix elements. Indeed, several corrections to ETB have been proposed in such directions (see [4] and references therein).

Recently, a new ETB scheme has been presented that overcomes most of the above limitations [5]. It is based on a multipole expansion of the atomic potentials, which allows to introduce environment-dependent corrections to the Hamiltonian matrix elements based both on atomic species and atomic positions surrounding each atom.

II. Results and future developments

As shown in Fig. 1 for the examples of InGaSb and InAsSb, the scheme described before can reproduce alloy band gaps and bowing even where the parameterization of Jancu [3] fails, which is explained mainly by increased transferability.

The gain in fidelity is paid, however, by a distinct increase in number of empirical parameters and a more complex fitting procedure. In fact, the complete family of materials, like (Al,Ga,In)(As,P,Sb), should be fitted at once, because the bare onsite parameters have to be consistent, and all necessary combinations of binary materials need to be described. As an alternative, we explored the possibility to employ Machine Learning (ML) to learn environment dependent corrections to

This work received funding from the European Union's Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement n° 956548, project QUANTIMONY, under NextGenerationEU Italian National Center 1 on HPCSpoke 6: 'Multiscale Modelling and Engineering Applications' MUR CUP: E83C22003230001, and under PON Ricerca e Innovazione—FSE REACT-EU9.

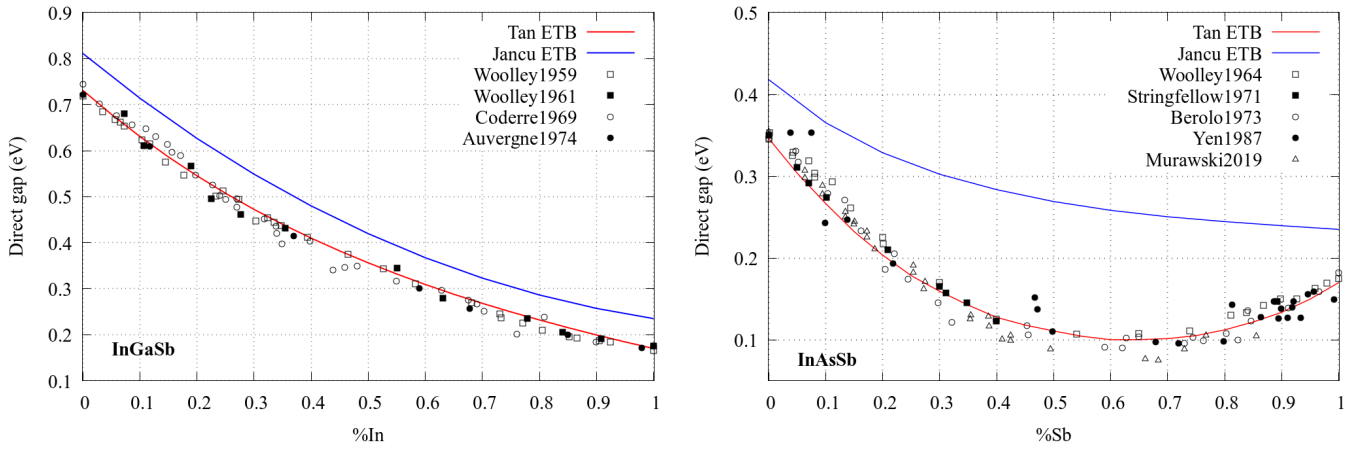

Fig. 1. Band gap of InGaSb (left) and InAsSb (right) alloys, calculated with ETB schemes from [3] (blue) and [5] (red), in comparison with experimental data. The energy shift is due to the fact that Jancu's parameters are fitted for 0 K. Figures are from [4] under Creative Commons CC-BY.

the ETB Hamiltonian obtained using a standard parameterization [6]. After the critical step of identifying a suitable descriptor using moment tensors, a neural network has been trained on a minimal set of DFT calculations on small alloy supercells. The output values of the network in our test implementation were the four diagonal, orbital-wise energy corrections. We have observed that this approach allows to reliably reproduce the band gap bowing, as shown for the example of GaAsSb in Fig. 2, even though the training data itself due to the small supercell size did not reproduce the correct bowing. Note that also in this case Jancu's parameterization heavily underestimates bowing.

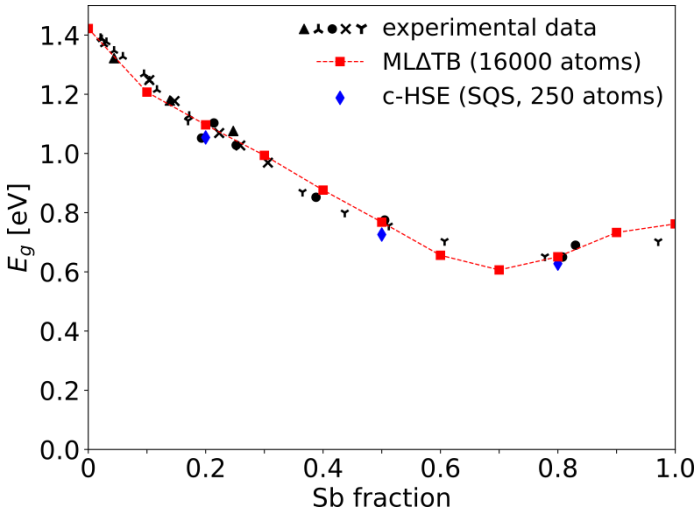

Fig. 2. Band gap of GaAsSb calculated with a machine-learning corrected ETB scheme (red), compared with experimental data and DFT calculations. Figure taken from [6] under Creative Commons CC-BY.

This shows the importance of environment-dependent corrections also in the onsite blocks of the ETB Hamiltonian. As a conclusion, a reliable ETB scheme with predictive capability for alloy and heterostructure properties requires parameterizations beyond the standard schemes. In particular, a suitable environment dependency is needed, which can be obtained either by expanding the parameter set and improving physical meaning of the empirically calculated Hamiltonian matrix elements, or by directly learning local corrections. In this latter case, it appears that the training space is not necessarily large. In both cases, the parameterization requires care, in order to guarantee the required transferability.

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