Modeling electronic and optical properties of III–V quantum dots—selected recent developments

Alexander Mittelstädt1, Andrei Schliwa1✉ and Petr Klenovský2,3

Abstract
Electronic properties of selected quantum dot (QD) systems are surveyed based on the multi-band \( \textbf{k} \cdot \textbf{p} \) method, which we benchmark by direct comparison to the empirical tight-binding algorithm, and we also discuss the newly developed “linear combination of quantum dot orbitals” method. Furthermore, we focus on two major complexes: First, the role of antimony incorporation in InGaAs/GaAs submonolayer QDs and In\(_{1-x}\)Ga\(_x\)As\(_y\)Sb\(_{1-y}\)/GaP QDs, and second, the theory of QD-based quantum cascade lasers and the related prospect of room temperature lasing.

Introduction
Semiconductor quantum dots (QDs) are a customized synthetic equivalent to atoms that have found uses in a wide range of modern semiconductor devices1. Nanostructures based solely on III–V-system material compounds provide already a wide spectrum of electronic and optical characteristics. This article will demonstrate their immense potential and tunability by concentrating on the electronic structure of three unique keystone systems of today’s research: (i) Sb-InAs/GaAs submonolayer QDs, (ii) In\(_{1-x}\)Ga\(_x\)As\(_y\)Sb\(_{1-y}\)/GaP QDs and (iii) QD based quantum cascade lasers.

(i) For the last 20 years\(^2,6\), InAs/GaAs QDs have been the focus of comprehensive research, leading to the development of quantum dot lasers\(^7\) and single-photon emitters\(^2,8\). To increase QD density and improve carrier dynamics, submonolayer quantum dots (SML QDs) were developed as a complementary approach for QD formation\(^9,10\): Deposition of fewer than one monolayer (ML) of InAs on GaAs, followed by a small spacer layer of GaAs, is repeated multiple times to form a submonolayer stack. In this paper, we discuss how Sb, as a further atomic species, affects the optical and electronic properties of InAs/GaAs submonolayer stacks.

(ii) One of the major challenges of future photonics\(^11\) is the monolithic integration of III-V compounds with silicon technology: GaP is the III-V binary compound with the nearest lattice constant to silicon (0.37 percent lattice mismatch at room temperature) and—despite being an indirect semiconductor—works well as a matrix for the In\(_{1-x}\)Ga\(_x\)As\(_y\)Sb\(_{1-y}\) material combination, which is discussed here for its potential as an optoelectronic material or its suitability as a storage element. To this purpose, we use an extended version of our previous model that includes X- and L-point states now.

(iii) Suris suggested quantum cascade lasers (QCL) having an active zone made of quantum dot (QD) chains in 1996\(^12\). Despite their enormous prospective, their realization has so far been delayed mostly by a lack of fast and accurate electronic structure modeling tools for large ensembles of closely aligned QDs. For this reason, we have established the “linear combination of quantum dot orbitals” (LCQO) approach and used it to the construction of a terahertz QD-QCL which lase at room temperature.
Due to the necessity for both fast and precise electronic structure calculations, 3D QD models that go beyond effective mass theory were developed, where simulations based on eight-band kp theory are among the most transparent ones. The attractiveness of the multi-band kp model stems from the appealing balance of accuracy, computation speed, and clarity of the physics and parameters employed. For any geometry and composition, all important aspects such like confinement, strain, piezo- and pyroelectricity, band-coupling, and -splitting may be faithfully addressed. This brings up the possibility of using the model for inverse bandstructure modeling and inverse design.

**Method of calculation**

The modeling approach used in this paper is depicted schematically in Fig. 1. It begins with the definition of a 3D QD morphology and continues with strain, piezoelectricity, and pyroelectricity calculations. The strain and polarization fields that arise are subsequently passed into the 8-band kp Hamiltonian. The single-particle states are calculated by solving the Schrödinger equation. The configuration interaction method, which is based on either the original single-particle states or Hartree-Fock modified states, can be used to account for Coulomb interaction. Finally, optical parameters including absorption spectra, capture cross-sections, and lifetimes can be determined. To keep the reasoning focused, we do not discuss excitonic effects in this work.

**Calculation of strain**

Because the strain impact on confinement is equivalent to the band offset caused by chemical composition variations at heterojunctions, the energies and wavefunctions are substantially influenced by the associated strain distribution. Several studies have looked at the suitability of the continuum elasticity model utilized to generate the strain distribution in our kp model: The continuum elasticity model, according to Stier et al., provides more reliable outcomes for QDs compared to Keatings valence force field (VFF) model in its linearized Kane version, where large parts of the strain distribution differences are ascribed to an incorrect elastic constant value C44 in the VFF model, rather than its atomistic nature. Zunger et al. later proposed the G-VFF model, a modified version of the VFF model that correctly incorporates C44. For the lattice relaxation, more recent versions of the tight-binding model use Stillinger-Webber and Abel-Tersoff force field potentials.

Because the kp model includes a restricted number of parameters only to incorporate strain, it is not receptive to the entire information provided by an atomistic strain model; hence, the continuum model remains the best choice in the context of our electronic structure model.

**Piezoelectricity**

The creation of electric polarization by applying stress to a crystal that lacks a center of symmetry is known as piezoelectricity. The zincblende structure is the most basic example of this kind of lattice, with one constant, e14, for the linear and three constants, B114, B124, and B156 for the quadratic terms, yielding:

\[
P_1 = 2 \epsilon_{14} (\epsilon_{yz} \epsilon_{xz} \epsilon_{xy})
\]

\[
P_2 = 2 B_{114} (\epsilon_{yz} \epsilon_{xz} \epsilon_{yy} \epsilon_{xx} \epsilon_{zz} \epsilon_{yy})
\]

\[
+ 2 B_{124} (\epsilon_{yz} (\epsilon_{yy} + \epsilon_{zz}) \epsilon_{zz} (\epsilon_{xx} + \epsilon_{yy}) \epsilon_{xy} (\epsilon_{xx} + \epsilon_{yy}))
\]

\[
+ 2 B_{156} (\epsilon_{yz} \epsilon_{xx} \epsilon_{yz} \epsilon_{yy} \epsilon_{xx} \epsilon_{xy})
\]

The resulting polarization \( P_{zb} \) then comprises of two components

\[
P_{zb} = P_1 + P_2
\]

Bester et al. have highlighted the relevance of the second-order term \( P_2 \) for InGaAs/GaAs(111) quantum wells (QW) and quantum dots (QDs). They discovered that the linear and quadratic coefficients have opposing impact on the potential for QWs, and that the quadratic term prevails for large strain.

The problem, however, is much deeper for InGaAs/GaAs QDs because, further to the enormous strain, their three-dimensional morphology is involved: A quadrupole-like potential is generated by the linear term, which reduces a QD’s structural \( C_{4v} \)– or \( C_{m} \) -symmetry to \( C_{2v} \). Bester et al. investigated the
effect of the quadratic terms on circular-shaped QDs and discovered that they compensate the first-order field inside the QD, resulting in a potential-free QD. Later, the research was expanded to include more realistic morphologies such as truncated pyramids and uneven alloyings.

Piezoelectric fields accumulate at the first and last QD positions of a stack of vertically aligned QDs and tend to cancel in the center area. Figure 2 depicts the increase in the first and second-order piezoelectric potential with increasing number of QDs (a) for one QD, (b) a pair of two QDs, and (c) a batch of ten QDs, as it may occur in the context of QD based QCLs. The piezoelectric potential is derived by numerically solving the Poisson equation (using Dirichlet boundary conditions) and then adding it as a mean-field to the envelope-function eight-band kp Hamiltonian for each grid cell.

**Eight-band kp method: one-particle states**

Using the 8-band kp model in real space and non-periodic boundary conditions, the energy levels and wavefunctions of bound electron and hole states are computed. Originally, the idea was developed to describe electronic states in bulk materials. The theory’s envelope-function variant has been further refined and applied to heterostructures such as quantum wells, quantum wires, and quantum dots. Ref. explains the rationale behind our approach for zinc blende heterostructures.

This model allows us to consider the impact of strain, piezoelectricity, valence band (VB) mixing, and conduction (CB)-VB interaction on QDs of any geometry and material composition. The predictions of the 8-band kp theory are constrained to the Brillouin zone center’s local vicinity owing to the restricted number of Bloch functions utilized for the wavefunction expansion. However, as previously stated, we compute off-center states using the effective mass model: The envelope function approach is used to generate one-particle states for X and L electron states, and the following equation is solved:

\[
\hat{H}^{L,X} F(r) = EF(r)
\]

where \( E \) and \( F(r) \) denote the eigenenergy and their associated envelope function, and \( \hat{H}^{L,X} \) is provided by

\[
\hat{H}^{L,X} = -\frac{\hbar^2}{2m^*(r)} \nabla + E_i^{L,X}(r) + V_{ext}(r)
\]

Here, \( E_i^{L,X}(r) \) is the L or X point’s position-dependent bulk conduction band energy, \( V_{ext}(r) \) denotes the external potential generated by, for example, elastic strain.

The amplitude of the strain-induced band shifts is determined by the material-dependent deformation potentials. The resulting energy shift at the CB \( \Gamma \) point, and the valleys at the L and X points, then reads:

\[
E_i^{\Gamma}(\vec{k}, \varepsilon) = E_i^{\Gamma}(\vec{k}_0) + \sum_{j} E_j^{\Gamma}(\varepsilon) + \sum_{i} E_i^{\Gamma}(\vec{k}_0 \cdot \varepsilon \vec{k}_0)
\]

with the absolute \( E_j^{\Gamma} \) and the uniaxial \( E_i^{\Gamma} \) deformation potentials, \( i \in \{ \Gamma, X, L \}; \varepsilon \) denotes the strain.

Meanwhile, an 8-band kp implementation for zinc blende and wurtzite QDs is provided through the nextnano project and is employed herein discussing (InGa)(AsSb)/GaAs/GaP quantum dots.

**Comparison to the sp\textsuperscript{3}s\textsuperscript{4} empirical tight-binding method**

In order to benchmark our kp model, we set up a state-of-the-art sp\textsuperscript{3}s\textsuperscript{4} empirical tight-binding (ETB) model. This model has atomistic resolution but considers only a minimal atomic basis, allowing large systems to be computed with high precision in a reasonable time. Similar to kp-ETB was developed in the past for full-Brillouin zone description of bulk electronic structure. In ETB, the Schrödinger equation is solved, similarly as for kp-ETB wavefunctions are also envelopes, yet in a basis of atomic orbitals or crystal Bloch waves. Generally, the larger number of basis atomic orbitals is used, the larger part of kp-space is reproduced by ETB correctly.
The usually used bases are sp\(^3\)s~*\(^{42}\) and sp\(^3\)d\(^5\)s~*\(^{43}\). The ETB Hamiltonian \(\hat{H}_{ETB}\) is composed of diagonal so-called "on-site" terms related to orbital atomic eigenenergies and off-diagonal ones, called "hopping" terms, related to the interaction between the atomic orbitals of the atom under consideration with its atomic neighbors.

Again, increasing the distance to which the hopping interaction is considered, i.e., the number of neighbors, increases the precision of ETB. Usually, nearest neighbors (NN) or next-nearest neighbors are considered. Since we use an ETB method with orthogonalized atomistic orbitals, it is enough to take into account only interaction with NNs.

The general pattern of constructing Hamiltonian in ETB and \(k\cdot p\) methods is somewhat similar: diagonal matrix terms include atomic (for ETB) or Bloch wave (for \(k\cdot p\)) eigenenergies and off-diagonal matrix terms are composed of interactions between atomic orbitals (for ETB) or Bloch states (for \(k\cdot p\)). Unlike envelope-function \(k\cdot p\) theory, which computes the electronic states of electrons and holes in a 3D quantum well, in ETB those are interwoven with states of bulk. That complicates their identification, e.g., for nanostructures, as those are "inner" eigenstates of the ETB Hamiltonian and not the ground state.

In the model used, spin–orbit interaction, piezoelectricity and strain are also considered. While piezoelectricity or external electric fields are accounted for in ETB similarly as in \(k\cdot p\) described earlier, elastic strain is calculated at the atomistic level using the molecular dynamics simulator LAMMPS\(^{43}\) and non-linear Stillinger–Webber potentials of the VFF model\(^{46}\). The resulting differences to the unstrained atom positions are realized in ETB model by the direction cosines in the Slater-Koster formulas (angle change) and Harrison’s power law (distance change). For the calculation of the highest occupied and lowest unoccupied states of the InAs QD, calculations at the gamma point and with a sp\(^3\)s~* basis per atom provide accurate results. In order to obtain eigenenergies and eigenfunctions we diagonalized ETB matrix using the PETSc/SLEPc numerical package\(^{47,48}\). Further details of the model used can be found in the Supplementary information and refs. \(^{49–55}\).

We compare the results of envelope-function eight-band \(k\cdot p\) and ETB for a typical InAs QD in GaAs matrix with a 0.5 nm InAs wetting layer, see Fig. 3. The \(k\cdot p\) computations were performed using Nextnano simulation suite\(^{40}\), including the calculation of elastic strain by CM model.

The parameters for \(k\cdot p\) are from the library of Nextnano\(^{40}\) and the orthogonal ETB parameters are taken from refs. \(^{49,50}\). For simplicity, piezoelectricity was not considered for calculations in Fig. 3.

One can clearly deduce from Fig. 3 that the results obtained using ETB and eight-band \(k\cdot p\) are very similar. The differences observed there are mainly due to the dot shapes not exactly matching each other between those methods.

Furthermore, given that sp\(^3\)s~* ETB (i) suffers from an inherent ambiguity\(^{56}\) of onsite elements at heterostructure interfaces necessitating to use the virtual crystal approximation to restore matrix Hermiticity, (ii) fails to correctly reproduce energies and effective masses\(^{43}\) at Brillouin zone edges (see Fig. 3a), and (iii) is computationally much more expensive than eight-band \(k\cdot p\) (i.e., \(\sim20\) h@16 CPU vs. \(\sim1\) h@1CPU computation time on a standard computer for ETB and \(k\cdot p\), respectively), we find the former not to provide significant advantages over the eight-band \(k\cdot p\). The only advantage of the ETB is that it preserves the QD’s correct \(C_{2v}\) symmetry of the underlying zincblende lattice owing to its atomistic nature.

**Coupled quantum dots and larger systems**

To make simulations of large systems with twenty and more electronically coupled QDs more economical, we introduce a new “linear combination of atomic orbitals” type of approximation. Our derivation, the LCQO approach operates along the following principle (See Fig. 4): First, a library of QDs is developed, methodically spanning diverse sizes, shapes, and chemical composition profiles, as well as the related one-particle states. Subsequently, motivated by the specified target properties, arrangements of vertically aligned QDs are built, together with the related Hamilton operator. The latter is then expanded into the basis of one-QD eigenstates as previously stored in our library.

The approach described herein employs basis functions derived using an eight-band \(k\cdot p\) model with realistic structures, strain, and strain-induced internal potentials. Compared to a complete eight-band \(k\cdot p\) calculation for a couple of two QDs, the resulting LCQO eigenstates and -energies exhibit good agreement, as shown in Fig. 5, indicating that the LCQO approach offers reliable results equivalent to those obtained from a full-scale \(k\cdot p\) simulation.

Using the LCQO technique, we can account for the unique 3D morphology of each QD inside the stack, as well as strain and strain-induced internal potentials of the entire system together with inter-dot electronic coupling. The method is introduced and further outlined in Mittelstädt et al.\(^{57}\) and can be implemented in conjunction with any continuum or atomistic model employed to determine single-particle states.

Benchmarking for an exemplary system of twenty one-particle states in a series of ten QDs demonstrates that the LCQO technique reduces computing time by at least three orders of magnitude.
Discussion of selected topics
Submonolayer QD systems: antimony-driven strong charge-carrier localization

Quantum physics and engineering of III-Sb materials and devices are currently flourishing worldwide. With the development of completely new applications, III-Sb will facilitate volume production of consumer products with improved performance and functionality, such as terahertz transceivers for future 5G mobile systems or low-voltage, low-energy, non-volatile “universal” memories. Energy harvesting green technologies may benefit from the developments of III-Sb-based multi-junction solar cells surpassing the 50% efficiency barrier. Beyond “classical” CMOS, information and communication technologies are now entering the quantum era. Here too, the intriguing electronic and magnetic properties of III-Sb are playing a fundamental role in infrared quantum light sources, spin–photon interfaces, and other quantum communication and information processing devices.

Submonolayer systems are an excellent illustration of how antimony addition may aid to tune the electronic structure and shift emission to longer wavelengths:
The cyclic deposition of tiny islands of InAs onto a GaAs matrix results in the development of a customized rough quantum well with densely spaced Indium-rich agglomerations that promote efficient exciton creation.

Antimony alloying improves carrier localization even further, since even modest quantities of Sb incorporation have a huge impact on the arrangement of conduction and valence band positions. Submonolayer QDs exhibit QD-like ultrafast carrier dynamics while also having a much higher modal gain, approaching values seen in InGaAs quantum-well structures.

The extent of hole localization, which is greatly enhanced by the addition of antimony, is the primary difference between alloyed and unalloyed submonolayer quantum dots. As a result, the alloyed submonolayer quantum dots may be used to provide heterodimensional confinement, ranging from totally zero- to heterodimensional confinement with completely confined holes and electrons unbound in two dimensions.

Adding antimony during growth can affect the carrier confinement InAs SML QDs. The influence of Sb alloying on electron and hole wavefunctions was studied employing multi-band k·p simulations for three distinct Sb inclusion arrangements:

A. Antimony incorporation into the quantum dots (Fig. 6b)
B. Antimony is distributed evenly within the SML structure (not displayed)
C. Antimony deposition between the quantum dots (Fig. 6c).

Based on earlier data from structural analysis, the simulation’s basic structure is composed of an 8.5 nm...
thick InGaAs QW with 15% Indium content. Embedded into this QW are circular In-rich accumulations with a \( \cos^2 \) composition profile, a peak local indium content of 35%, and a separation of 13.6 nm.

To begin with, introducing antimony into the SML stack results in a shift to lower energies of the PL emission in all three considered scenarios, with the largest shift being 140 meV in case (B). To generate a comparable redshift in the other two situations, a maximum Sb content of higher than 20% is required.

As the band alignment scheme in Fig. 7 shows, electron and hole wavefunctions behave highly different when it comes to antimony incorporation: Hole states localize in antimony-rich areas, whereas electron states prefer indium-rich regions and delocalize from antimony-rich regions (Fig. 7b).

The electric dipole moment in the semiconductor structure is influenced by the spatial distribution of the wavefunctions; their overlap defines the Huang-Rhys factor\(^5^9\), which is also a metric of LO phonon coupling. A smaller Huang-Rhys factor results from better overlap of the wavefunctions. Figure 7a depicts the band lineup for the three alternative Sb incorporation assumptions, as well as the case without Sb.

In case (A), the incorporation of antimony into QDs causes the hole wavefunction to become more localized, whereas the electron wavefunction delocalizes (Fig. 7a, b). This causes a significant reduction in electron–hole overlap, resulting in a 15-fold rise in the Huang-Rhys factor from 0.005 without Sb to 0.076 at a peak local Sb level of 20%.

An equal distribution of antimony across the SML structure, as in case (B), results in somewhat larger delocalization of the hole wavefunction (Fig. 7b), resulting in stronger overlap and, as a result, a lower Huang-Rhys factor of only 0.001 for 10% antimony content. Case (C), in which antimony is inserted between the QDs, causes the hole wavefunction to be localized at the antimony-rich areas (Fig. 7b), resulting in a substantial delocalization from the QDs; as a result of the decreased overlap, the Huang-Rhys factor increases to 0.018 for 20% Sb content. This scenario corresponds to the smallest total strain in the SML nanostructure.

A comprehensive examination of the PL spectra in ref. \(^5^8\) reveals a coupling strength indicating case (A) to be the most plausible, i.e., a preferred incorporation of antimony in the SML QDs, as well as a shift to lower emission energy for different cases of Sb incorporation in or beside In-rich regions and hole localization at Sb-rich regions. The structural analysis findings also demonstrate that antimony is located in or immediately at the sidewalls of the indium-rich agglomerations (ref. \(^5^8\)), resulting in situations similar to scenario (A).

**(InGa)(AsSb)/GaAs/GaP—k-indirect transitions**

Future information technologies will have to rely on dedicated components that make full use of the quantum
technologies. While QDs from III–V compounds were identified as being nearly ideal in that sense, complications arise with integrating those with current mature Si technology\textsuperscript{19}. One of the main problems is the sizeable lattice offset between QD semiconductor materials and Si. While that issue can be overcome by gradually growing almost lattice-matched compounds on Si, that approach is technologically complicated and tedious (i.e., necessity of elaborate growth protocols). Thus, it would be favorable to find a semiconductor material with lattice constant close to that of Si. Fortunately, from III–V binary compounds that property is fulfilled by GaP since its lattice is mismatched to that of Si by only 0.37% at 300 K. Sadly, since GaP has the lowest energy transition between conduction and valence band indirect in k-space, it cannot be considered useful for construction of light sources. However, it can be used as buffer for growth of other, more appropriate material combinations. First, InGaP alloy was tested in the past for usage as an active material, but it failed due to its type-I to type-II band offset to GaP\textsuperscript{60}. On the other hand, \((\text{In, Ga})\text{As}/\text{GaP}\) shows type-I confinement and was also studied considerably using theory and experimental methods\textsuperscript{64–67}. However, that alloy still has a large lattice mismatch to GaP, leading to huge built-in strain, possibly causing a crossover of the ground-state transition from k-direct to k-indirect in \((\text{In, Ga})\text{As}/\text{GaP}\). The necessary fraction of In leading to type-I direct electron-hole transition in \((\text{InGa})(\text{AsN})/\text{GaP}\) was found by Fukami et al.\textsuperscript{68} using model-solid theory.

Later on, Robert et al.\textsuperscript{69–71} predicted a change of k-direct to k-indirect transition for ~30% In concentration for bigger \((\text{In, Ga})\text{As}\) QDs in GaP using a mixed k-p/ETB theory. Interestingly, for smaller QDs they identified an even larger In content for that transition.

Triggered by the experimental works of Sala et al.\textsuperscript{72,73}, we\textsuperscript{74} researched the role of further antimony incorporation, i.e., we studied the electronic structure of \(\text{In}_{1-x}\text{Ga}_x\text{As}_{1-y}\text{Sb}_{y}/\text{GaP}\) QDs. We have looked not only at its appropriateness for optoelectronic materials\textsuperscript{75} but also as material for QD-Flash memories that combine long retention time with fast read/write capability, as previously proposed by Sala et al.\textsuperscript{73}. Moreover, we note that a fair amount of theory work on Sb containing InAs QD structures was done in the past\textsuperscript{76–82} as well as for QDs with k-indirect transitions\textsuperscript{83} and the study of the present system is a natural expansion of that.

Since GaP substrate causes huge compressive strain in our QDs, in the \(\text{In}_{1-x}\text{Ga}_x\text{As}_{1-y}\text{Sb}_{y}/\text{GaP}\) system the k-indirect electron states are found at smaller energies than those for \(\Gamma\). That is in striking difference to more traditionally used QD systems like, e.g., \((\text{In, Ga})\text{As}\) QDs in GaAs. Furthermore, because the L (X) bulk Bloch waves have eight- (six-) fold symmetry, there are four (three-) L (X) envelope functions of quasiparticles in this QD system, each state related to two neighboring Brillouin zones. Hence, those envelope wave functions are called \(L(110), L(-110), L(1-10), \text{and} L(-1-10)/X(100), X(010), \text{and} X(001)\).

When Eq. (1) is evaluated along QD symmetry-line (and for negligible shear strain, i.e., \(\varepsilon_{xy} = \varepsilon_{xz} = \varepsilon_{yz} = 0\)), one finds that

\[
\begin{align*}
E^L_c([100], e) &= E^L_c + a^L_c tr(e) \\
E^L_c([111], e) &= E^L_c + a^L_c tr(e) + \frac{1}{3} a^L_{cu}(\varepsilon_{xx} + \varepsilon_{yy} + \varepsilon_{zz}) \\
E^X_c([100], e) &= E^X_c + a^X_c tr(e) + a^X_{cu}(\varepsilon_{xx}) \\
E^X_c([010], e) &= E^X_c + a^X_c tr(e) + a^X_{cu}(\varepsilon_{yy}) \\
E^X_c([001], e) &= E^X_c + a^X_c tr(e) + a^X_{cu}(\varepsilon_{zz})
\end{align*}
\]

where \(a_c\) and \(a_{cu}\) are the absolute deformation potential and the uniaxial shear deformation potential in [100]-direction of the conduction band, respectively. While the term for \(E^L_c([111], e)\) is the same for all L-points, a splitting occurs between \(E^X_c([100], e)\), \(E^X_c([010], e)\), and \(E^L_c([001], e)\). However, for QD’s symmetry-line, \(\varepsilon_{xx} = \varepsilon_{yy}\) and, thus, \(E^X_c([100], e)\), \(E^X_c([010], e)\), and \(E^L_c([001], e)\) are identical (see Fig. 8).

However, in real \(\text{In}_{1-x}\text{Ga}_x\text{As}_{1-y}\text{Sb}_{y}/\text{GaP}\) QDs, the degeneracy of envelopes for \(L(110), L(-1-10), L(1-10), \text{and} L(-110)/X(100), X(010), \text{and} X(001)\) is canceled because of structural asymmetries (e.g., shape, composition) and/or due to externally applied perturbations (e.g., strain, magnetic, or electric). That effect of degeneracy lifting is studied in Fig. 9 for carefully chosen exemplary points, A, B, C, and D, exhibiting specific properties.

The shape and size of our modeled QDs are related to that found by Stracke and Sala\textsuperscript{2,73} and was recently confirmed by cross-sectional scanning tunneling microscopy (XSTM) and atom probe tomography (APT) measurements\textsuperscript{84}, see Fig. 9(f) for the whole structure with 5-ML GaAs interlayer (IL) between QD and GaP substrate.

The local band-edges, computed without and with considering the elastic strain, are shown in Fig. 8a, revealing the vast impact strain has on our system’s confinement properties: In all cases (see also ref. \textsuperscript{74}), we observe a k-direct to k-indirect transition of the QD-confinement. Antimony incorporation further diversifies the picture, and a real-space type-I to type-II transition for \(\Gamma\)-states emerges (Fig. 9e), being a perfect pre-requisite for the QD-Flash memory concept. Furthermore, we note that our model is applicable also in strong and weak confinement regime.

We finally note that the results of our calculations were recently confirmed using detailed power-, temperature-, and time-resolved photoluminescence measurements\textsuperscript{73,85}.

### QD based quantum cascade lasers and temperature stability

QCLs are unipolar laser devices wherein electrons run down a staircase potential staircase built from a quantum
well (QW) superlattice, and lasing is achieved via intra-band transitions. A concept proposed already in 1971 by Kazarinov and Suris.\textsuperscript{86} Despite remarkable advances in material research that resulted in temperature records reported by Bosco et al.\textsuperscript{87} and more recently by Khalatpour et al. in ref.\textsuperscript{88} however, room temperature operation remains unattained. The operating temperature is limited on the one hand by an increased competition of radiative transitions with nonradiative scattering losses and absorption of
free carriers\textsuperscript{89–91}, and on the other hand by a challenging injection of carriers into the upper laser level for transitions at energies below the longitudinal optical phonon frequency of the material (less than 20 meV), so-called terahertz (THz) QCLs. In particular, population inversion is degraded by the continuous subbands in 2-D heterostructures, favoring nonradiative scattering of electrons from the upper laser level and the lower laser level’s thermal backfilling. Since the carriers in the conduction band can easily relax into a lower subband by emitting a phonon, these nonradiative decay processes are much faster than the radiative ones\textsuperscript{92–94}, resulting in generally high threshold current densities of QCL devices (∼kA cm\textsuperscript{-2}), irrespective of the laser’s transition energy.

To overcome these shortcomings, in 1996 Suris developed the idea of using chains of quantum dots as gain material for quantum cascade lasers (QD-QCLs)\textsuperscript{95,99–101}. Such lasers were predicted to benefit from the inherently narrow gain spectrum, reduced electron–phonon relaxation (phonon bottleneck), and free-carrier absorption of QDs, significantly enhancing carrier lifetimes\textsuperscript{96–98} and thus improving temperature stability with significantly reduced threshold current densities\textsuperscript{55,99–101}. Moreover, the operating voltages in conventional QCLs are rather high because the tunneling barriers between adjacent QWs need to be small to form a superlattice. By using QD chains, in contrast, interdot barriers can be selected larger, as the wavefunction penetration in the growth direction is much larger than for comparable QW structures. Consequently, the mutual overlap of the wavefunctions of adjacent QDs is larger than for QW structures with identical spacings, allowing the voltage to be smaller, reducing parasitic tunneling.

A further advantage of using QDs is their anisotropic radiation pattern, enabling the design of surface-emitting lasers based on strong vertical emission of s-to-p-like intraband transitions. Then, THz QD-QCLs, in particular, would benefit from a facile coupling into optical fibers, low-cost production, and high output powers by operation in arrays.

**Proposal for a room-temperature THz laser**

We present a QD chain’s band structure calculation featuring an intraband staircase potential with a laser transition in the THz regime. The THz QCL design comprises an array chain built from 20 stacked InGaAs QDs embedded in a GaAs matrix forming a two-QD unit-cell superlattice; see Fig. 10. Delocalized electronic states resulting from strong electronic interdot coupling are tailored to enable occupation inversion at a specific range of external biases. With the help of transport calculations built on the calculated band structures and device parameters mapped from experiments, we find a significantly reduced threshold current density and higher temperature stability compared to QW-based cascade lasers.

The computational cost of finding a suitable QD gain material is less the calculation of (1) the electronic structure of large-scale finite QD systems, but scales primarily with the computation of (2) dozens of electronic states of these QD chains and the (3) numerous iterations required to arrive at a suitable bandstructure design. The latter are, therefore, the major challenges in a design study. Thereby, the morphology, composition, length of the QD chain, and width of the tunneling barriers of the QDs along the QD chain, which affects the interdot coupling strength, were varied to arrive at a promising band structure. The realization of a QCL requires a meticulous band structure design. In particular, this requires, on the one hand, cascaded intraband transitions of matched energy and shared carrier probability densities of neighboring QDs and, on the other hand, in- and out-scattering rates allowing population inversion between the laser levels. In an extensive parameter study, using the results and discussions in ref. \textsuperscript{57} and our newly developed LCQO method, we have investigated more than one hundred possible realizations of QD chains within experimentally realistic parameters at various external biases. The QD-QCL active region consists of In\textsubscript{0.7}Ga\textsubscript{0.3}As QDs electronically coupled via tunneling barriers of width \( b \) and modeled as truncated pyramids, following transmission electron microscopy investigations of Stranski-Krastanov QDs\textsuperscript{102,103}.

Our design uses a two-QD unit cell with QDs coupled across an 8 ML barrier, where barriers of 20 MLs separate neighboring unit cells. Consequently, the densities within the two-QD unit-cells are well localized and the overlap of carrier densities from cascade to cascade is reduced accordingly, minimizing the leakage current from the upper laser level and facilitating population inversion. The band structure is motivated by designs.

![Fig. 10 Scheme of a vertical-cavity surface-emitting QD chain-based QCL. a Electronically coupled QDs form an array of QD chains serving as the QCL's gain material. b QDs separated by tunneling barriers of width \( b \) arranged in two-QD unit cells. c Vertical spontaneous emission from transitions between s-type (blue) and p-type (green) QD orbitals](image-url)
already used in QW-based QCLs that attained record temperatures; cf. refs. 87,91,104,105.

Figure 11 shows a segment of the QD chain’s band structure, resulting in seven cascades along the 20 QD chain. There are seven laser transitions between the unit cells and four QDs at the top and bottom; cf. the Supplemental Material of ref. 57. The arrows indicate the laser transition, and the orbitals involved are displayed in the inset. Shown are two cascades of the QD chain, which consists of seven in total. The applied external bias voltage is set to 46 kV/cm.

Conclusions

In this article, we provided an overview on the envelope-function-based eight-band $k\cdot p$ method and the newly developed “linear combination of quantum dot orbitals” method for electronic structure calculations of small and large systems of QDs. Furthermore, we have benchmarked our $k\cdot p$ method against an atomistic sp$^3$s* empirical tight-binding algorithm, which we have set up, finding it a fast and reliable alternative to its atomistic counterpart.

Furthermore, three types of heterostructures of current relevance are utilized to demonstrate the $k\cdot p$ approaches’ broad range of application:

(i) the electronic and optical properties of InAs/GaAs submonolayer stacks with Sb as an extra atomic species—enabling significant shifts of the emission to longer wavelengths,

(ii) In$_{1-x}$Ga$_x$As$_2$Sb$_{1-y}$ lattice-matched to GaP, thus, possibly paving the path to monolithic integration of III–V compounds with Si technology, and

(iii) the application of our newly developed LCQO method and its application to the design of a terahertz QD-QCL, aiming at lasing at room temperature. The LCQO method enables and accelerates the computation of the band structure of QD stacks QD stacks with 20 or more QDs, including dozens of electronic states, at an affordable computational cost while maintaining the accuracy provided by the eight-band $k\cdot p$ method.

Acknowledgements

Many coworkers contributed to the accomplishment of this project. We are especially grateful for the contributions of Oliver Stier, Marius Grundmann, Momme Winkelnkemper, Steffen Westerkamp, Ludwig Greif, Stefan Jagsch, and...
and Vlastimil Křapek, as well as the support by Dieter Bimberg. P.K. would like to thank Miroslav Valtír and Petr Klápeta from the Czech Metrology Institute for providing their supercomputer computational resources for running the ETB code. A.S. is partially funded by the MSc-ITN-2020 Funding Scheme from the European Union’s Horizon 2020 program under Grant agreement ID: 956548 (Quantumy). Nextnano, in particular Stefan Birner, is acknowledged for providing their software for parts of this work (nextnano++) and for their kind support. P.K. was financed by the project CUSPIODR and has received funding from the QuantERA ERA-NET CoFund in Quantum Technologies implemented within the European Union’s Horizon 2020 program and from the MEYS of the Czech Republic under grant agreement ID: 731473. The work reported in this paper also was partially funded by projects 20INDS05 QADeT, 20FUnSQ2D SEQUENCE and 17FUnSQ2D Sigmat that received funding from the EMPIR program co-financed by the Participating States and from the European Union’s Horizon 2020 research and innovation program.

Author details
1Institute for Solid State Physics, Technical University of Berlin, Hardenbergstrasse 36, D-10623 Berlin, Germany. 2Department of Condensed Matter Physics, Faculty of Science, Masaryk University, Kotlárská 267/2, 61137 Brno, Czech Republic. 3Czech Metrology Institute, Okružní 31, 63800 Brno, Czech Republic

Funding
Open Access funding enabled and organized by Projekt DEAL.

Competing interests
The authors declare no competing interests.

Supplementary information
The online version contains supplementary material available at https://doi.org/10.1038/s41377-021-00700-9.

Received: 6 April 2021 Revised: 5 November 2021 Accepted: 16 December 2021 Published online: 17 January 2022

References
1. Bimberg, D., Grundmann, M. & Ledentsov, N. N. Quantum Dot Heterostructures. 328 (New York: John Wiley, 1999).
2. Schimpf, C., Mann, S., da Silva, S. F. C., Agnier, M. & Ratelli, A. Entanglement-based quantum key distribution with a bina
ing-free quantum dot operated at a temperature up to 20 K. Advanced Photonics 3, 065001-1-065001-7 (2021).
3. Huber, D. et al. Single-particle-picture breakdown in laterally weakly confining GaAs quantum dots. Phys. Rev. B 100, 235425 (2019).
4. Huang, H. et al. Electric field induced tuning of electronic correlation in weakly confining quantum dots. Phys. Rev. B 80, 165401 (2009).
5. Csontosivá, D. & Klenovský, P. Theory of magneto-optical properties of neutral and charged excitons in GaAs/AlGaAs quantum dots. Phys. Rev. B 82, 125412 (2010).
6. Grundmann, M., Steir, O. & Bimberg, D. InAs/AlGaAs pyramidal quantum dots: strain distribution, optical phonons, and electronic structure. Phys. Rev. B 52, 11981 (1995).
7. Korda, D. et al. Strong threshold, large T, injection laser emission from InGaAs quantum dots. Electron. Lett. 30, 1416–1417 (1994).
8. Michler, P. et al. A quantum dot single-photon tunable device. Science 290, 2282–2285 (2000).
9. Milhkin, S. S. et al. 0.94 μm diode lasers based on Stranski-Krastanov and sub-
monolayer quantum dots. Semiconductor Sci. Technol. 15, 1061–1064 (2000).
10. Owczynikow, N. et al. Submonolayer quantum dots. Semiconductor Nanophotonic. Mater., Models, Devices 194, 13 (2020).
11. Liang, D. & Bowers, J. E. Recent progress in lasers on silicon. Nat. Photonics 4, 511–517 (2010).
12. Suris, R. A. Prospects for quantum dot structures applications in electronics and optoelectronics. In Future Trends in Microelectronics (eds Lyuty, S., Xu, J. & Zelidovik, A.), pp. 197–208 (Dordrecht: Springer, 1996), https://doi.org/10.1007/978-94-009-1746-0_17
13. Jiang, H. T. & Singh, J. Strain distribution and electronic spectra of InAs/GaAs self-assembled dots: an eight-band study. Phys. Rev. B 56, 4966–4971 (1997).
14. Shi, A., Hong, G. & Bimberg D. Electronic properties of In-Ga-As quantum dots. Multi-Band Effective Mass Approximations. Springer, Cham, 57–85 (2014).
15. Steir, O., Grundmann, M. & Bimberg, D. Electronic and optical properties of strained quantum dots modeled by 8-band k·p theory. Phys. Rev. B 59, 5688–5701 (1999).
16. Shi, A., Winkelnkemper, M. & Bimberg, D. Few-particle energies versus geometry and composition of InGaAs–AlGaAs self-organized quantum dots. Phys. Rev. B 79, 075443 (2009).
17. Minar, V. & Junger, A. Effect of atomic-scale randomness on the optical polarization of semiconductor quantum dots. Phys. Rev. B 79, 115416 (2009).
18. Honig, G. et al. Manifestation of unconventional biexciton states in quantum dots. Nat. Commun. 5, 5721 (2014).
19. Ambacher, O. et al. Electronics and sensors based on pyroelectric AlGaN/GaN heterostructures. Phys. Status Solidi (b) 268, 1878–1907 (2003).
20. Williamson, A. J., Wang, L. W. & Junger, A. Theoretical interpretation of the experimental electronic structure of self-assembled InAsGaAs quantum dots. Phys. Rev. B 62, 12963 (2000).
21. Stilling, F. H. & Weber, T. A. Computer simulation of local order in condensed phases of silicon. Phys. Rev. B 81, 5262 (1985).
22. Tersoff, J. Modeling solid-state chemistry: Interatomic potentials for multi-
component systems. Phys. Rev. B 39, 5666 (1989).
23. Cady, W. G. Piezoelectricity: An Introduction to the Theory and Applications of Electromechanical Phenomena in Crystals. (McGraw-Hill, 1946).
24. Bester, G. et al. Importance of second-order piezoelectric effects in zinc-
blende semiconductors. Phys. Rev. Lett. 96, 187602 (2006).
25. Bester, G. & Junger, A. Cylindrically shaped zinc-blende semiconductor quantum dots do not have cylindrical symmetry: atomic deformation, atomic relaxation, and piezoelectric effects. Phys. Rev. B 71, 045318 (2005).
26. Bester, G. et al. Effects of linear and nonlinear piezoelectricity on the electronic properties of InAs/GaAs quantum dots. Phys. Rev. B 74, 081305 (2006).
27. Shi, A., Winkelnkemper, M. & Bimberg, D. Impact of size, shape, and composition on piezoelectric effects and electronic properties of InGaAs/
GaAs quantum dots. Phys. Rev. B 82, 045414-1-045414-6 (2017).
28. Averb, J. et al. Inversion of the exciton built-in dipole moment in InGaAs quantum dots via nonlinear piezoelectric effect. Phys. Rev. B 96, 045414-1-045414-6 (2017).
29. Klenovský, P. et al. Effect of second-order piezoelectricity on the excitonic structure of stress-tuned InGaAs quantum dots. Phys. Rev. B 97, 245314 (2018).
30. Kane, E. O. Band structure of indium antimonide. J. Phys. Chem. Solids 1, 249–261 (1957).
31. Pollak, F. H. Effects of homogeneous strain on the electronic and vibrational levels in semiconductors. Semicond. Semimet. 32, 17–53 (1990).
32. Enk, T. et al. k.p theory of energy bands, wave functions, and optical selection rules in strained tetrahedral semiconductors. Phys. Rev. B 51, 16695–16704 (1995).
33. Gershoni, D., Henry, C. H. & Baraff, G. A. Calculating the optical properties of multidimensional heterostructures: application to the modeling of quan-
tum-quantum well lasers. IEEE J. Quantum Electron. 29, 2433–2450 (1993).
34. Steir, O. & Bimberg, D. Modeling of strained quantum wires using eight-band k·p theory. Phys. Rev. B 55, 7726–7732 (1997).
35. Taylor, C. Eight-band calculations of strained InAs/GaAs quantum dots compared with one-, four-, and six-band approximations. Phys. Rev. B 57, 7190–7195 (1998).
36. Majewski, J. A. et al. Advances in the theory of electronic structure of semiconductors. Phys. Status Solidi (b) 1, 2003–2027 (2004).
37. Zibold, T. Semiconductor Based Quantum Information Devices: Theory and Simulations. PhD thesis, Technische Universität München, München, 2007.
38. Bardeen, J. & Shockley, W. Deformation potentials and mobilities in non-polar crystals. Phys. Rev. J. Arch. 80, 72–80 (1950).
39. Hering, C. & Vogt, E. Transport and deformation-potential theory for many-
valley semiconductors with anisotropic scattering. Phys. Rev. 101, 944–961 (1956).
40. Birner, S. et al. nextnano: general purpose 3D simulations. IEEE Trans. Electron Devices 7, 5137–5142 (2007).
41. Trellakis, A. et al. The 3D nanometer device project nextnano: concepts, methods, results. J. Comput. Electron. 5, 285–289 (2006).
101. Vukmirovic, N. et al. Electron transport and terahertz gain in quantum-dot cascades. *IEEE Photonics Technol. Lett.* **20**, 129–131 (2008).

102. Blank, H. et al. Quantification of the In-distribution in embedded InGaAs quantum dots by transmission electron microscopy. *Cryst. Res. Technol.* **44**, 1083–1088 (2009).

103. Litvinov, D. et al. Influence of InGaAs cap layers with different In concentration on the properties of InGaAs quantum dots. *J. Appl. Phys.* **103**, 083532 (2008).

104. Franckié, M. et al. Two-well quantum cascade laser optimization by non-equilibrium Green’s function modelling. *Appl. Phys. Lett.* **112**, 021104 (2018).

105. Kumar, S. et al. A 1.8-THz quantum cascade laser operating significantly above the temperature of $\hbar \omega/k_B$. *Nat. Phys.* **7**, 166–171 (2011).

106. Mittelstädt, A. et al. Terahertz lasing at room temperature: a numerical study of a vertical-emitting quantum cascade laser based on a quantum dot superlattice. *Phys. Rev. B* **103**, 115301 (2021).

107. Ulbrich, N. et al. Intersubband staircase laser. *Appl. Phys. Lett.* **80**, 4312–4314 (2002).

108. Kumar, S. et al. Two-well terahertz quantum-cascade laser with direct intrawell-phonon depopulation. *Appl. Phys. Lett.* **95**, 141110 (2009).

109. Scalari, G. et al. Broadband THz lasing from a photon-phonon quantum cascade structure. *Opt. Express* **18**, 8043–8052 (2010).