

SILICON NANOWIRE-BASED COMPLEX STRUCTURES: A LARGE-SCALE ATOMISTIC ELECTRONIC STRUCTURE AND BALLISTIC TRANSPORT

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August, 2014

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ABSTRACT

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PhD in Physics

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While the hierarchical assembling as well as the dramatic miniaturization of Si nanowires (NWs) are on-going, an understanding of the underlying physics is of great importance to enable custom design of nanostructures tailored to specific functionalities. This work presents a large-scale atomistic insight into the electronic properties of NW-based complex structures, starting from the subsystem level up to the full assembly, within the framework of pseudopotential-based linear combination of bulk bands method. Laying the groundwork by grasping single Si NWs, we get into a large extent an unexplored territory of NW networks and kinked NWs. As one end product, a versatile estimator is introduced for the band gap and band-edge lineups of multiply-crossing Si NWs that is valid for various diameters, number of crossings, and NW alignments. Aiming for an exploration of the low-lying energy landscape, real space wave function analysis is undertaken for tens of states around band edges which reveal underlying features for a variety of crossings. Predominantly, the valence states spread throughout the network, in contrast the conduction minima are largely localized at the crossings. Given the fact that substantial portion of the band edge shift drives from the confined conduction states, branched Si NWs and nanocrystals have quite close band gap values as the networks of similar wire diameters. Further support to wave function analysis is provided via quantum ballistic transport calculations employing the Kubo-Greenwood formalism. The intriguing localization behaviors are identified, springing mainly at the crossings and kinks of NWs. The ballistic transport edge set apart the conducting extended states from the localized-band gap determining ones. Our findings put forward useful information to realize functionality encoded synthesis of NW-based complex structures, both in the bottom-up and top-down fabrication paradigms.

Keywords: Silicon nanowire, nanowire networks, kinked nanowires, electronic structure, band edge alignments, linear combination of bulk bands, quantum ballistic transport, Kubo-Greenwood formula.

ÖZET

SİLİSYUM NANOTEL TABANLI KARMAŞIK YAPILAR: BÜYÜK ÖLÇEKLİ ATOMİK ELEKTRONİK YAPI VE BALİSTİK TAŞINIM

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Silisyum nanoteller ve bu nanotelleri temel alarak geliştirilen daha karmaşık yapılar, yeni kuşak nano-aygıtlarda esas yapıtaşları olarak kullanılmaya başlanmıştır. Ancak uygulamadaki ilerleyişinin hızına karşılık, nanotel temelli karmaşık yapıların kuramsal fiziği pek de incelenmemiştir. Oysaki bilhassa elektriksel ve taşınım özelliklerinin kavranması hem kuramsal bağlamda kuantum etkilerin küçük boyutlardaki tipik davranışlarına ışık tutacak hem de uygulama alanında ileride yapılacak yeni aygıtların olası davranışları ve sınırları için öngörü oluşturabilecektir. Buradan hareketle, çalışmamızda tekil nanotellerden başlayarak; nanotel kavşakları, tel ağları ve dirsekli teller aşamalı olarak irdelenmiştir. Öncelikle adı geçen büyük ölçekli nano-sistemlerin elektronik yapıları ve bu kapsamda bant aralıkları ile bant kenarı hizalanmaları, atomik görünürpotansiyel temelli yığın bantların doğrusal birleştirimi yöntemi ile çıkarılmıştır. İncelenen malzemelerin boyutu küçülürken, iletim bant kenarı değeri, değerlik bant kenarına göre daha fazla değişmektedir. Elde edilen sonuçlar ışığında, ikili ve üçlü kavşaklar için farklı çap değerlerine göre enerji aralığı ve bant hizalanmalarının öngörülmesini sağlayacak genel bir uyum fonksiyonu ortaya konulmuştur. Devamında, nanoyapıların dalga fonksiyonlarının kareleri üzerinden yük yoğunlukları ve yük yoğunluklarının karmaşık nanotel yapılarındaki yerleşmeleri incelenmiştir. Genellikle düşük enerjili iletim durumları kavşak ve dirsek bölgelerinde yerleşirken, değerlik durumları nanoyapının geneline yayılma özelliği göstermektedir. Bu gözlem, bant aralığının daha ziyade iletim kenarının kaymasıyla olduğu sonucuyla birleştirildiğinde nanotel ağları için bulduğumuz sonuçların aynı çaplı dallanmış nanokristal ve nanoteller için de geçerli olduğu gözlemlenmiştir. Yük yerleşmelerinin fiziksel etkilerini daha fazla

kavrayabilmek için elektriksel iletim hesaplamaları yapılmıştır. İletim bant kenarı, yerleşmiş enerji durumları ile malzeme boyunca ilettime açık olan yayılmış durumları birbirinden ayırmaktadır. Yerleşmiş enerji durumları, kesişen ve dirsekli nanotellerin enerji bant aralığını belirlediği halde iletim daha yüksek enerji değerlerinde başlamaktadır. Bulgularımız kuantum sınırlama etkisinin karmaşık nanotel temelli yapılarda oynadığı önemli rolü ortaya koymuş ve ayrıca bu malzemelerin uygulamaları için faydalı öngörüler sağlamıştır.

Anahtar sözcükler: Silisyum nanotel, nanotel ağları, dirsekli nanotel, balistik elektriksel iletkenlik, elektronik yapı hesabı, yığın bantların doğrusal birleşimi, görünürpotansiyel yöntemi, bant kenarı hizalanması, Kubo-Greenwood gösterimi, kuantum sınırlama etkisi.

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to the memory of Ayça Erem Bulutay...

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Chapter 1

Introduction

Semiconductor nanowires (NWs) are functional building blocks at the forefront of nanoscience and nanotechnology due to their controllable synthesis, confined carriers, tunable indirect-to-direct band gaps, and high surface-to-volume ratios [12, 13, 14]. Though the appearance of NWs can be traced back to the whiskers of 1960s [15, 16, 17], the bloom of both experimental and theoretical research waited till 1990s for the striking photoluminescence properties of porous silicon (PS) [18, 19]. One of the explanations of blue shift in PS was presented by modeling PS as an array of Si NWs [18, 19, 20, 21, 22, 23]. Shedding light on the quantum size effect and hence the band gap engineering opportunities, the success of the model heralded the promising future of NWs.

Si NW architectures, among all semiconductors, have the upper hand thanks to their inherent integrability and compatibility with the native silicon technology. Single-crystalline Si NWs have been synthesized with various diameter distributions, growth orientations and dopant concentrations with various techniques [24, 25, 26, 27, 28, 1, 29]. The advancements in ability to rationally synthesize Si NWs has enabled several applications such as biosensors [30], logic gates [31], lasers [32], electronic [33], photonic [34], photovoltaic [35, 36], and thermoelectric devices [37, 38].

In particular, the transistor applications of Si NWs have received wide spread

attention. As the channel length of conventional metal-oxide-semiconductor field-effect-transistors (MOSFETs) shrinks down to nanometer regime, the performance enhancement by further downscaling becomes questionable mainly due to the short-channel effects [39, 40]. In order to continue the effective miniaturization as captured by Moore’s law [41], the complementary MOS technology seeks new device architectures in which the bulk MOSFETs are replaced by convenient alternatives. In this regard, Si NW transistors promise a possible solution to the downscaling challenges of MOSFETs thanks to their enhanced electrostatic controllability and close to the ballistic limit transport capabilities [39]. The reliable fabrications of SiNW FETs have been demonstrated by several experimental studies with NW diameters reaching down to several nanometers [33, 42, 43, 44, 45, 46, 47, 48].

In the sub-10-nm dimension scale, the quantum effects substantially alter the bulk electronic properties and hence the conventional transport features, giving rise to modified band structures, indirect-to-direct band gap transitions, quantized conductance, and interference effects, just to name a few. Nevertheless, due to the experimental difficulties in determining the electronic properties of nanostructures [49], it becomes vital to predict them via realistic computational tools. Having a solid understanding of the underlying physics, one can suggest design principles to achieve specific functionalities and indicate the potential performance limits.

Various electronic structure calculation methods have been applied to understand the material properties of Si NWs. Particularly, the structure and surface chemistry-dependent electronic properties such as wire diameter, cross-section shape, growth orientation, surface passivation and doping profile are widely investigated [20, 50, 4, 51, 52, 6, 53, 8, 9, 54, 55, 3]. A comprehensive review on the theoretical investigations about structural, electronic, and transport properties of Si NWs is given by Rurali [14]. Majority of the theoretical studies have been performed within the first principles density functional theory (DFT) [20, 50, 4, 51, 52, 6, 53, 8, 9, 54]. Corrections to the underestimated Kohn-Sham energy gap [56] are introduced by GW approximation [4, 6, 5, 7], hybrid functionals [8, 9] or scissor operation [10]. Alternatively, the electronic

properties can also be computed with the empirical [55, 57, 2, 58] and semiempirical [3] methods. These latter methods, with reduced computational load, enable access to Si NWs with diameters reaching up to 10 nm [58].

Among many possible device applications of NWs, the transistors stands at the forefront due to the industrial demands. Therefore, it is not surprising that many of the theoretical efforts on Si NWs have focused on their transport characteristics. Different electronic structure methods have been exploited such as the effective mass approximation, with [59, 60, 61, 62] and without [63, 64, 65, 66, 67, 68, 69, 70, 71, 72, 73, 74, 75, 76, 77, 78] non-parabolic band corrections, $\vec{k} \cdot \vec{p}$ method [79, 80], tight binding approach [66, 81, 82, 83, 75, 84, 85, 86], and first principles calculations [87, 88, 89], to name a few. Then the resulting band structure information is used to feed the transport calculations, relying on semiclassical ballistic model [83], compact modeling [73, 89, 77], multisubband Monte Carlo technique [60, 74, 75], direct solution of Boltzmann transport equation [62, 71, 70, 85], Kubo-Greenwood formula [63, 76], Landauer-Büttiker formula [87, 88, 61, 82, 89], or nonequilibrium Green's function (NEGF) method [64, 65, 67, 81, 68, 69, 82, 72, 74, 84, 78, 80]. Ballistic transport is expected to play an important role in the electronic performance of NW-based devices [90, 91, 64, 67, 68, 61, 83, 70, 72, 73, 89, 80]. On the other hand, several scattering mechanism can limit the transport, including surface roughness scattering [65, 87, 59, 60, 69, 62, 71, 72, 75, 84, 85, 76, 78, 80] as well as phonon [63, 67, 59, 60, 62, 85, 80], Coulomb [59, 76], and impurity [88, 62, 74, 75, 85] scattering. Strain engineering [81, 86, 80] techniques can also significantly modify the device performance.

Once the controllable synthesis and physical understanding of NWs advances, as a natural next step, there has been a considerable interest in assembling them into higher dimensional hierarchical architectures as functional building blocks for the next generation devices. En route, after the introduction of branched nanocrystals [92], the branched [93] or tree-like [94] epitaxial NW structures are immediately realized. This is followed by the interconnection of branched nanostructures into the large-scale NW networks, in some cases employing different semiconductors [95, 96].

In addition to significant progress achieved in their controllable growth [97, 98], branching structures have been introduced as key components of nanoelectronic devices including light-emitting diodes, logic gates, and biosensors [98]. Branching nanostructures are also discussed and suggested as a central material for the implementation of third-generation photovoltaics, as the branching structures improve the light absorption by the increase of absorbing medium, in comparison to conventional NW solar cells; moreover, reduce the light reflectance with increasing the effective path for scattered light to travel within the network [99]. In particular, Si NW networks are employed in the fabrication of thermoelectric devices [100], photodetectors [101], and, biosensors [102]. The realization of other proposals, such as multi-terminal electron devices and artificial neural networks are still waiting for the implementation [96, 103].

Yet, there appears to be very limited understanding of the underlying mechanism to tune the electronic properties of NW *networks*. More critically, to take the best advantage, fundamentals of carrier collection, separation and transport processes need to be clarified. Besides, the band alignments of these nanostructures are essential for a proper electrical contact design to effectively extract the carriers. Thus, the paradigm brought by branched nanowires for assembling hierarchical devices makes it essential to understand the novel physical phenomena in nanoscale crossing-wire structures. By this way, one can address how will the promising NW utilities will be taken over to networks and will networks reveal even *new* features?

Nevertheless, in contrast to the single SiNWs, only a few theoretical studies have been carried out for the electronic properties of branched Si NWs and NW networks. Menon *et al.* [104] investigate the branched pristine Si NWs, whereas experimentally grown NWs have always passivated surfaces. Avramov *et al.* [105] consider some very small size flower-like Si nanoclusters rather than realistic branched Si NWs. In regard to electronic transport in NW networks, since seminal work of Büttiker [106], many studies have been conducted in the context of quantum transport in multi-terminal junctions, Refs. [107, 108, 109, 110, 111] to name some. Moreover, the NW junctions formed by putting one NW on top

of another one is investigated within a lattice tight binding model in conjunction with the Green's function approach [112]. This work indicates bound and quasi-bound states at around the contact region as a consequence of interwire interaction. The intra- and inter-wire couplings are included with some representative parameters. Nevertheless, to the best of our knowledge none of the aforementioned works in this field has considered the proper atomistic treatment of NWs. The lack of more realistic theoretical treatment in such an experimentally attractive area can be explained by the fact that even the smallest realistic branched systems, including the surface passivation media, contains $\sim 10^3$ – 10^4 atoms in the computational supercell. Though, DFT-based calculations set the benchmark reference for electronic structure calculations, the computational load increases intractably for the realistic branched materials. Therefore, the comprehensive study of realistic branched structures stands as a great challenge for the first principles methods due to prohibitively increased computational load and requires more feasible semiempirical techniques.

1.1 This Work

The aim of this work is to shed light on several issues raised above, from a theoretical-computational perspective. We present a large-scale atomistic insight into the electronic properties of Si NW-based complex nanostructures, mainly to the networks of Si NWs. This has been achieved by focusing on two aspects: the electronic band structures and quantum ballistic transport. Although these two subjects are Siamese twins, their characteristics extensions invoke separated treatments. In Chapters 2 and 3, we concentrate on the electronic structure calculations. In Chapters 4 and 5, we spotlight the quantum transport features.

Nanostructures are model systems to investigate the manifestations of quantum effects due to their unprecedented dimension scales, crystalline purity and perfection. Nevertheless, the experimental limitations on measuring the electronic structure call realistic theoretical tools to assess the fundamental features.

In our computational framework, the semiempirical pseudopotential-based *atomistic* Hamiltonian is solved using an expansion basis formed by the linear combination of bulk bands (LCBB) of the constituents of the nanostructure, i.e., Si and embedding matrix in our case. The formulation of the method and its implementation details as well as convergence tests are given in Chapter 2. Being a semiempirical method, LCBB has the advantage that the calculated band gaps of nanostructures reasonably agree with the experimental values whenever available. Yet, the main virtue of the method is that it allows us to deal with systems containing tens of thousands of atoms within a reliable accuracy at the band edge energy landscape.

In Chapter 3, we report our electronic structure results. First, to lay the groundwork for NW networks, we consider embedded Si NWs oriented in $\langle 100 \rangle$, $\langle 110 \rangle$, $\langle 111 \rangle$, and $\langle 112 \rangle$ crystalline directions. We compute the band gap energies as well as valence and conduction band edge alignments with respect to those of bulk Si as a function of NW diameter. Our results are compared with the literature whenever available. In order to interpret the calculated band structures, the Brillouin zone folding and indirect-to-direct band gap transitions are discussed. This is followed by a detailed analysis of Si NW networks, composed by regular arrays of NW-crossings, to construct the understanding of their electronic properties. The comprehensive results are consolidated into a general expression which provides an effective way to estimate the electronic band gaps of NW networks. Considering device applications, the band-offsets of Si NWs and NW networks with respect to the band edges of bulk Si and SiO₂ are also provided.

To gain more insight into the underlying physics of NW networks and further NW-based complex nanostructures such as kinked NWs, in Chapters 4 and 5, we complement the electronic structure calculations with quantum ballistic transport and carrier localization analysis. Accordingly, in Chapter 4, first we give a preliminary discussion of 1D ballistic transport in the context of Landauer formula. Then, in the seek of a fully quantum mechanical representation, we derive the Kubo-Greenwood (KB) formula. In the subsequent sections, we indicate the computational implementation details of KG-formula and examine the bridging with the LCBB method. Finally, we revisit the convergence of LCBB calculated

band structure in the light of conductance calculations.

In Chapter 5, after briefly visiting the transport features of single NWs, we proceed with the analysis of isosurfaces of carrier densities to address the impact of crossings and kinks on the electronic behavior. The carrier localization analysis are interpreted together with the ballistic transport calculations to derive conclusions on the characteristic features of NW-based complex nanostructures. Based on our results on the band edges and charge profiles, we assert that the results derived for networks are general and apply as well to branched nanocrystals and branched NWs.

To conclude, in Chapter 6, we summarize and discuss our results. We indicate some open questions for the future works. In Appendix A, we show the calculation of momentum matrix elements within the context of LCBB method. Appendix B demonstrates some numerical implementation details of KG-formula on a toy model.

Chapter 2

Mise en scène: Linear Combination of Bulk Bands Method

Reduction of the system dimensions to the nanoscale leads to intriguing quantum behaviors and impacts the device properties rather peculiarly. Due to experimental obstacles on measuring the electronic properties of nanostructures [49], it becomes vital to estimate the properties by means of reliable computational tools.

For the electronic structure calculations of large-scale nanostructure systems, Wang and Zunger introduced the linear combination of bulk bands method [113, 114, 115]. The method suggests to expand the states of considered nanostructure in terms of full-zone bulk Bloch bands of the underlying materials, i.e., Si and silica in our case. The main virtue of the method lies in the construction of the expansion basis. The insightful selection of the basis economizes that, and thus enabling to compute even million-atom systems [115]. Basing on a semiempirical pseudopotential Hamiltonian, moreover, the LCBB method embraces the fine details of the atomistic environment.

The idea of exploiting the bulk bands in the expansion basis can be traced

back to the works of Ninno *et al.* [116, 117]. Following Wang and Zunger’s formulation for self-assembled quantum dots [114, 115, 118] several different groups have successfully implemented the method for various systems such as superlattices [119, 120], high-electron mobility transistors [121], Si inversion layer [122], and embedded Si and Ge nanocrystals [123, 124, 125, 126, 11].

LCBB method is originally introduced for the electronic structure calculations of nanocrystals [114, 115]. By this reason, the formulation and implementation details of LCBB are often given for the three-dimensional (3D) supercell case which inherently bases on a 3D reciprocal space representation [114, 115, 123]. In the case of 1D nanostructures, only two of the three translational symmetries are broken, in comparison to nanocrystals, revealing energy dispersion along the continuum direction. In order to compute the proper energy dispersion relation, one needs a modified planar expansion basis set and corresponding separated eigenvalue problems. In this chapter, we emphasize the elaboration of the latter, the organization is such that: in Sec. 2.1, we present the formulation of LCBB method and some guidelines for the computational implementation. An important aspect of the electronic structure computations is the surface passivation. We describe our passivation recipe in Sec. 2.2. Further details on the expansion basis selection as well as convergence tests are given in Sec. 2.3.

2.1 Formalism

In the wave function expansion methods [56], the states of the nanostructures $\Psi_j(\vec{r})$ are expressed as a linear combination of appropriate basis functions,

$$\Psi_j(\vec{r}) = \sum_{\alpha=1}^{N_\alpha} C_{\alpha,j} \phi_\alpha(\vec{r}), \quad (2.1)$$

where the quantities $C_{\alpha,j}$ are the expansion coefficients. Form of the basis functions are specified by the particular method applied, plane waves, Wannier functions or atomic orbitals, just to name a few [56]. The number N_α of basis functions $\phi_\alpha(\vec{r})$ scales linearly with system size (i.e., the number of atoms) such that the expansion becomes quickly intractable for large-size nanostructures [115]. In this

regard, the LCBB method proposes to overcome this handicap by forming an economic expansion basis which is formed with insightful choices.

As an antecedent to LCBB method, we can consider the $\vec{k} \cdot \vec{r}$ method in which the zone-center Γ ($\vec{k} = 0$) bulk Bloch bands $\{u_{n,0}(\vec{r})\}$ are employed to form the expansion basis $\{\phi_\alpha(\vec{r}) = u_{n,0}(\vec{r})e^{i\vec{k} \cdot \vec{r}}\}$. Then the states of the nanostructure can be expanded as

$$\Psi_j(\vec{r}) = \sum_{n,\vec{k}}^{N_B, N_k} C_{n,\vec{k},j} \left[u_{n,0}(\vec{r}) e^{i\vec{k} \cdot \vec{r}} \right], \quad (2.2)$$

where N_B is the number of bands and N_k is the number of wave vectors $\vec{k}$ included in the expansion. The inevitable error of the approach is that it is not possible to generate the full-band structure through the Brillouin zone (BZ) unless all ($N_B = \infty$) zone-center bulk bands are included [114].

In the LCBB method, the zone-center bands $\{u_{n,0}\}$ in Eq. (2.2) are replaced with the full-zone bulk Bloch bands $\{u_{n,\vec{k}}\}$ of the underlying semiconductors of the nanostructure. Within this framework, the nanostructure states can be written as the linear combination of bulk bands, rewriting Eq. (2.2), we get the expansion

$$\Psi_j(\vec{r}) = \sum_{n,\vec{k},\sigma} C_{n,\vec{k},j}^\sigma \phi_{n,\vec{k}}^\sigma(\vec{r}) = \sum_{n,\vec{k},\sigma} C_{n,\vec{k},j}^\sigma \left[\frac{1}{\sqrt{N}} u_{n,\vec{k}}^\sigma(\vec{r}) e^{i\vec{k} \cdot \vec{r}} \right], \quad (2.3)$$

where N is the number of bulk primitive unit cells within the large supercell of the nanostructure, n is the bulk band index, $\vec{k}$ is the wave vector belonging to the first BZ of the underlying lattice, and σ is the underlying material index. The periodic part $u_{n,\vec{k}}^\sigma(\vec{r})$ of the bulk Bloch function can be expanded by the plane waves as

$$u_{n,\vec{k}}^\sigma(\vec{r}) = \frac{1}{\sqrt{\Omega_o}} \sum_{\vec{G}} B_{n\vec{k}}^\sigma(\vec{G}) e^{i\vec{G} \cdot \vec{r}}, \quad (2.4)$$

where N_G is the number of reciprocal lattice vectors (RLVs) $\vec{G}$ within an energy cut-off, and Ω_o is the volume of the primitive cell. The bulk expansion coefficients $B_{n\vec{k}}^\sigma(\vec{G})$ can be calculated by diagonalizing the bulk Hamiltonian for each $\vec{k}$ point. In our computational implementation, the bulk coefficients are computed by employing the empirical pseudopotential method (EPM) which is also very fast, accurate and easy to implement [127, 128]. Moreover, particularly unlike

ab initio calculations, EPM band gaps accurately agrees with the experimental values by its construction as they are fitted to bulk properties [127].

For the future reference, collecting all the terms, the LCBB expansion of nanostructure states can be expressed as:

$$\begin{aligned}\Psi_j(\vec{r}) &= \sum_{n,\vec{k},\sigma} C_{n,\vec{k},j}^\sigma \phi_{n,\vec{k}}^\sigma(\vec{r}) \\ &= \sum_{n,\vec{k},\sigma} C_{n,\vec{k},j}^\sigma \sum_{\vec{G}} \left[\frac{1}{\sqrt{V}} B_{n\vec{k}}^\sigma(\vec{G}) e^{i(\vec{k}+\vec{G})\cdot\vec{r}} \right],\end{aligned}\quad (2.5)$$

where $N\Omega_o = V$ is the volume of the computational supercell, being periodic in all three-dimensions.

The LCBB basis yields significant advantages: (i) The off- Γ bulk states ($u_{n,\vec{k}\neq 0}$) of the constituent materials can be directly included in the basis set. Thus, there is no need any more for huge number of Γ -states to be included into the expansion basis of Eq. (2.2). LCBB method differs in this respect from the $\vec{k}\cdot\vec{p}$ method. The full-band structure inherently comes out in LCBB method. (ii) Physically more relevant band-edge states are given the priority in the expansion basis. These benefits reduce the size of expansion basis and thereof result with the significantly lowered computational load. This computational efficiency allows us to consider systems with a very large number of atoms. The supercells containing tens of thousands of atoms are easily tractable with the LCBB method.

The total single-particle Hamiltonian of a generic nanostructure with the kinetic energy and the ionic potential parts, where the latter describes the atomistic environment within the pseudopotential framework, is expressed by

$$\hat{H} = \hat{T} + \hat{V}_{PP} = -\frac{\hbar^2 \nabla^2}{2m_o} + \sum_{\sigma, \vec{R}_l, \alpha} W_\alpha^\sigma(\vec{R}_l) v_\alpha^\sigma(\vec{r} - \vec{R}_l - \vec{d}_\alpha^\sigma). \quad (2.6)$$

Here m_o is the free electron mass, the direct lattice vector (DLV) $\vec{R}_l$ gives the position of the primitive cell and $\vec{d}_\alpha^\sigma$ specifies the relative coordinate of a particular atom within the primitive cell. The weight function $W_\alpha^\sigma(\vec{R}_l)$ keeps the information about the composition of the system by taking values 0 or 1 depending on the type of the atom located at the position $\vec{R}_l + \vec{d}_\alpha^\sigma$. v_α^σ is the local screened spherical

atomic pseudopotential of atom α of the material σ . In this work, we assume that all the materials forming the nanostructure have the same Bravais lattice. The generation of the method to strained systems can be found in Ref. [115].

In LCBB method, the Hamiltonian matrix elements are evaluated within the basis set $\{|n\vec{k}\sigma\rangle\}$ that is $\{\langle\vec{r}|n\vec{k}\sigma\rangle = \phi_{n,\vec{k}}^\sigma(\vec{r})\}$ in the position representation. The resulting Hamiltonian is diagonalized to yield $C_{n,\vec{k},j}^\sigma$ coefficients. The corresponding generalized eigenvalue problem is

$$\sum_{n,\vec{k},\sigma} \langle n'\vec{k}'\sigma'|\hat{T} + \hat{V}_{PP}|n\vec{k}\sigma\rangle C_{n,\vec{k},j}^\sigma = E_j \sum_{n,\vec{k},\sigma} C_{n,\vec{k},j}^\sigma \langle n'\vec{k}'\sigma'|n\vec{k}\sigma\rangle. \quad (2.7)$$

Let us consider the eigenvalue problem term by term. The right hand side term $\langle n'\vec{k}'\sigma'|n\vec{k}\sigma\rangle$ represents the bulk wave function overlap, inserting $\hat{I} = \int d^3r |\vec{r}\rangle\langle\vec{r}|$ into that, we get

$$\begin{aligned} \langle n'\vec{k}'\sigma'|n\vec{k}\sigma\rangle &= \frac{1}{N} \int_V d^3r \frac{1}{\sqrt{\Omega_o}} \sum_{\vec{G}'} B_{n'\vec{k}'}^{\sigma'}(\vec{G}')^* e^{-i(\vec{k}'+\vec{G}')\cdot\vec{r}} \frac{1}{\sqrt{\Omega_o}} \sum_{\vec{G}} B_{n\vec{k}}^\sigma(\vec{G}) e^{i(\vec{k}+\vec{G})\cdot\vec{r}} \\ &= \frac{1}{N} \int_V d^3r \frac{1}{\Omega_o} \sum_{\vec{G}',\vec{G}} B_{n'\vec{k}'}^{\sigma'}(\vec{G}')^* B_{n\vec{k}}^\sigma(\vec{G}) e^{i(\vec{k}-\vec{k}'+\vec{G}-\vec{G}')\cdot\vec{r}}. \end{aligned} \quad (2.8)$$

The position vector $\vec{r}$ of the supercell can be written as $\vec{r} = \vec{R}_l + \vec{r}_p$ where $\vec{R}_l$ are the DLVs of the lattice and $\vec{r}_p$ is the position vector inside the primitive cell. This allows us to write $\int_V d^3r \rightarrow \sum_{l=1}^N \int_{\Omega_o} d^3r_p$. Thus

$$\begin{aligned} \langle n'\vec{k}'\sigma'|n\vec{k}\sigma\rangle &= \sum_{\vec{G}',\vec{G}} B_{n'\vec{k}'}^{\sigma'}(\vec{G}')^* B_{n\vec{k}}^\sigma(\vec{G}) \frac{1}{N} \sum_{l=1}^N e^{i(\vec{k}-\vec{k}')\cdot\vec{R}_l} e^{i(\vec{G}-\vec{G}')\cdot\vec{R}_l} \\ &\quad \times \frac{1}{\Omega_o} \int_{\Omega_o} d^3r_p e^{i(\vec{G}-\vec{G}')\cdot\vec{r}_p}, \end{aligned} \quad (2.9)$$

using the facts that $\frac{1}{N} \sum_{l=1}^N e^{i(\vec{k}-\vec{k}')\cdot\vec{R}_l} = \delta_{\vec{k},\vec{k}'}$ and $\frac{1}{\Omega_o} \int_{\Omega_o} d^3r_p e^{i(\vec{G}-\vec{G}')\cdot\vec{r}_p} = \delta_{\vec{G},\vec{G}'}$, also since $e^{i(\vec{G}-\vec{G}')\cdot\vec{R}_l} = 1$, Eq. (2.9) yields

$$\langle n'\vec{k}'\sigma'|n\vec{k}\sigma\rangle = \delta_{\vec{k},\vec{k}'} \sum_{\vec{G}} B_{n'\vec{k}'}^{\sigma'}(\vec{G})^* B_{n\vec{k}}^\sigma(\vec{G}). \quad (2.10)$$

Notice that the term $\frac{1}{\Omega_o} \int_{\Omega_o} d^3r_p e^{i(\vec{k}-\vec{k}')\cdot\vec{r}_p}$ also drop here due to $\delta_{\vec{k},\vec{k}'}$. We employ those steps also in the kinetic energy matrix elements.

The next term kinetic energy matrix elements $\langle n' \vec{k}' \sigma' | \hat{T} | n \vec{k} \sigma \rangle$ in Eq. (2.7) can be treated similarly

$$\begin{aligned} \langle n' \vec{k}' \sigma' | \hat{T} | n \vec{k} \sigma \rangle &= \sum_{\vec{G}', \vec{G}} B_{n' \vec{k}'}^{\sigma'}(\vec{G}')^* B_{n \vec{k}}^{\sigma}(\vec{G}) \frac{\hbar^2 |\vec{k} + \vec{G}|^2}{2m_o} \frac{1}{N} \sum_{l=1}^N e^{i(\vec{k} - \vec{k}') \cdot \vec{R}_l} e^{i(\vec{G} - \vec{G}') \cdot \vec{R}_l} \\ &\quad \times \frac{1}{\Omega_o} \int_{\Omega_o} d^3 r_p e^{i(\vec{G} - \vec{G}') \cdot \vec{r}_p}, \quad (2.11) \end{aligned}$$

and thus gives

$$\langle n' \vec{k}' \sigma' | \hat{T} | n \vec{k} \sigma \rangle = \delta_{\vec{k}, \vec{k}'} \sum_{\vec{G}} \frac{\hbar^2 |\vec{k} + \vec{G}|^2}{2m_o} B_{n' \vec{k}'}^{\sigma'}(\vec{G})^* B_{n \vec{k}}^{\sigma}(\vec{G}). \quad (2.12)$$

The last term in Eq. (2.7) is the potential energy term $\langle n' \vec{k}' \sigma' | \hat{V}_{PP} | n \vec{k} \sigma \rangle$. To evaluate the matrix elements first inserting the identity vectors and then using the local pseudopotential property $\langle \vec{r} | \hat{V}_{PP} | \vec{r}' \rangle = \int \delta(\vec{r} - \vec{r}') V_{PP}(\vec{r}) d^3 r'$, we can write

$$\begin{aligned} \langle n' \vec{k}' \sigma' | \hat{V}_{PP} | n \vec{k} \sigma \rangle &= \frac{1}{N \Omega_o} \sum_{\vec{G}', \vec{G}} B_{n' \vec{k}'}^{\sigma'}(\vec{G}')^* B_{n \vec{k}}^{\sigma}(\vec{G}) \int_V d^3 r e^{i(\vec{k} + \vec{G} - \vec{k}' - \vec{G}') \cdot \vec{r}} \\ &\quad \times \sum_{\sigma'', \vec{R}_l, \alpha} W_{\alpha}^{\sigma''}(\vec{R}_l) v_{\alpha}^{\sigma''}(\vec{r} - \vec{R}_l - \vec{d}_{\alpha}^{\sigma''}), \quad (2.13) \end{aligned}$$

and with the change of variable $\vec{r} = \vec{R}_l + \vec{r}_p + \vec{d}_{\alpha}^{\sigma''}$, we obtain

$$\begin{aligned} \langle n' \vec{k}' \sigma' | \hat{V}_{PP} | n \vec{k} \sigma \rangle &= \sum_{\vec{G}, \vec{G}'} B_{n' \vec{k}'}^{\sigma'}(\vec{G}')^* B_{n \vec{k}}^{\sigma}(\vec{G}) \sum_{\sigma'', \alpha} \mathcal{V}_{\alpha}^{\sigma''}(|\vec{k} + \vec{G} - \vec{k}' - \vec{G}'|^2) \\ &\quad \times \mathcal{W}_{\alpha}^{\sigma''}(\vec{k} - \vec{k}') e^{i(\vec{k} + \vec{G} - \vec{k}' - \vec{G}') \cdot \vec{d}_{\alpha}^{\sigma''}}, \quad (2.14) \end{aligned}$$

where the discrete Fourier transforms are defined as

$$\mathcal{V}_{\alpha}^{\sigma''}(|\vec{k} + \vec{G} - \vec{k}' - \vec{G}'|^2) = \frac{1}{\Omega_o} \int_V v_{\alpha}^{\sigma''}(\vec{r}_p) e^{i(\vec{k} + \vec{G} - \vec{k}' - \vec{G}') \cdot \vec{r}_p} d^3 r_p \quad (2.15)$$

and

$$\mathcal{W}_{\alpha}^{\sigma''}(\vec{k} - \vec{k}') = \frac{1}{N} \sum_{\vec{R}_l} W_{\alpha}^{\sigma''}(\vec{R}_l) e^{i(\vec{k} - \vec{k}') \cdot \vec{R}_l}. \quad (2.16)$$

Here, we would like to *emphasize* an important *implementation detail* of LCBB method that derives from the definitions of the above discrete Fourier

transformations. As we state earlier, in this work the materials forming the nanostructure are assumed to have the same underlying Bravais lattice: $\vec{R}_{n_1, n_2, n_3} = n_1 \vec{a}_1 + n_2 \vec{a}_2 + n_3 \vec{a}_3$ where $\{\vec{a}_i\}$ are the primitive lattice vectors of the lattice. The 3D periodic boundary conditions dictate that

$$W(\vec{R}_{n_1, n_2, n_3} + N_i \vec{a}_i) = W(\vec{R}_{n_1, n_2, n_3}). \quad (2.17)$$

On the other hand, the discrete Fourier transformation introduced in the treatment of weight functions $\mathcal{W}_\alpha^{\sigma''}(\vec{q}) = \frac{1}{N} \sum_{\vec{R}_{n_1, n_2, n_3}} W_\alpha^{\sigma''}(\vec{R}_{n_1, n_2, n_3}) e^{i\vec{q} \cdot \vec{R}_{n_1, n_2, n_3}}$ requires $e^{i\vec{q} \cdot N_i \vec{a}_i} = 1$, so that the reciprocal space k-gridding should have the form

$$\vec{q} \rightarrow \vec{q}_{m_1, m_2, m_3} = \vec{b}_1 \frac{m_1}{N_1} + \vec{b}_2 \frac{m_2}{N_2} + \vec{b}_3 \frac{m_3}{N_3}, \quad (2.18)$$

where $\{\vec{b}_i\}$ are the reciprocal lattice primitive vectors of underlying bulk semiconductor and $m_i = 0, 1, \dots, N_i - 1$. Eq. (2.18) constitutes a strict relation between the real and reciprocal space grids. This relation is quite restrictive, in the sense that to increase the number of k-space sampling points (i.e., increasing N_i 's), one needs to enlarge the size of the supercell in real space due to Eq. (2.17). This procedure will inflate the computational load up to intractable limits. Concerning the rapid k-space convergence of LCBB, this is not a critical issue, nevertheless, it becomes crucial in the case of energy dispersion calculations.

For two-dimensionally confined nanostructures, e.g., NWs, only two of the three translational symmetries are broken, in comparison to nanocrystals, giving rise to the energy dispersion along the other direction. The band structure through the dispersion is essential to understand the physics of the material. In order to extract the energy dispersion at definite k-values along the translational symmetry, we should introduce a proper k-grid that both recognizes the dispersion direction and keeps the computational load tractable. This can be done by explicitly introducing the symmetry of the nanostructure to the LCBB formalism. In detail, considering the symmetry of the system, the three-dimensional real space (reciprocal space) can be separated into (i) planar two-dimensional space $\vec{r}_\perp$ ($\vec{k}_\perp$) coinciding with the perpendicular confinement plane, (ii) one-dimension space $\vec{r}_\parallel$ ($\vec{k}_\parallel$) parallel to the translational symmetry. Therefore, the vectors of three-dimensional real $\vec{r}$ (reciprocal $\vec{k}$) space can be separated into the components as: $\vec{r} = \vec{r}_\perp + \vec{r}_\parallel$ ($\vec{k} = \vec{k}_\perp + \vec{k}_\parallel$).

We would like to note that, as the LCBB Hamiltonian is constructed and solved in the reciprocal space, the k-space decomposition turns out to be more critical. Indeed, many of the nanostructures considered in this work enforce the employment of 3D real space, regarding the shape of the structures, whereas the reciprocal space can still be decomposed into perpendicular and parallel components. LCBB formalism has no restriction in this regard. Remarkably, as we are going to see in Ch. 5, the dual k-space treatment, 3D or separated 2D, allows us to gain a more complete understanding of some nanostructures.

The separated k-space approach requires a special treatment in the LCBB formalism. Let us briefly describe that. Following the real and reciprocal space decompositions, DLVs and RLVs can also be decomposed into parallel and perpendicular components: $\vec{R} = \vec{R}_{\parallel} + \vec{R}_{\perp}$ and $\vec{G} = \vec{G}_{\parallel} + \vec{G}_{\perp}$, respectively. Since we want the energy values at a definite $\vec{k}_{\parallel}$ value, we drop the sum over $\vec{k}_{\parallel}$ in Eq. (2.5). That leads to an expansion on a planar k-grid of $\vec{k}_{\perp}$:

$$\begin{aligned}\Psi_{j,\vec{k}_{\parallel}}(\vec{r}) &= \frac{1}{\sqrt{V}} \sum_{n,\vec{k}_{\perp},\sigma} C_{n,\vec{k}_{\perp},\vec{k}_{\parallel},j}^{\sigma} \sum_{\vec{G}} B_{n\vec{k}_{\perp}}^{\sigma}(\vec{G}) e^{i[(\vec{k}_{\perp}+\vec{k}_{\parallel})+\vec{G}]\cdot\vec{r}} \\ &= \frac{1}{\sqrt{V}} \sum_{n,\vec{k}_{\perp},\sigma} C_{n,\vec{k}_{\perp},\vec{k}_{\parallel},j}^{\sigma} \sum_{\vec{G}} B_{n\vec{k}_{\perp}}^{\sigma}(\vec{G}) e^{i(\vec{k}_{\perp}+\vec{G}_{\perp})\cdot\vec{r}_{\perp}} e^{i(k_{\parallel}+G_{\parallel})r_{\parallel}}. \quad (2.19)\end{aligned}$$

Here, in the summation $\vec{k}_{\parallel}$ still appears since it keeps the information that $\vec{k}_{\perp}$ is not always at the Brillouin center Γ , but can be shifted to a specific $\vec{k}_{\parallel}$ point along the Brillouin zone of the nanostructure.

Then the Schrödinger equation of LCBB changes from the general form of Eq. (2.7) to a specific form of definite $\vec{k}_{\parallel}$ such that

$$\begin{aligned}\sum_{n,\vec{k}_{\perp},\sigma} \langle n'\vec{k}'_{\perp}\vec{k}_{\parallel}\sigma'|\hat{T} + \hat{V}_{PP}|n\vec{k}_{\perp}\vec{k}_{\parallel}\sigma\rangle C_{n,\vec{k}_{\perp},\vec{k}_{\parallel},j}^{\sigma} = \\ E_j(\vec{k}_{\parallel}) \sum_{n,\vec{k}_{\perp},\sigma} C_{n,\vec{k}_{\perp},\vec{k}_{\parallel},j}^{\sigma} \langle n'\vec{k}'_{\perp}\vec{k}_{\parallel}\sigma', n\vec{k}_{\perp}\vec{k}_{\parallel}\sigma\rangle. \quad (2.20)\end{aligned}$$

This form does not put any restriction on our treatment of matrix elements. We should only need to form a planar k-grid at a specific $\vec{k}_{\parallel}$ point. This can be easily implemented in our coding by constructing a planar k-grid at Brillouin center,

i.e., $\vec{k}_{\perp,\Gamma}$ then carrying it to $k_{\parallel}$ point by $\vec{k} = \vec{k}_{\parallel} + \vec{k}_{\perp,\Gamma}$ (illustrated in Fig.2.6 of Sec. 2.3).

By switching to a planar k-grid and constructing the separated eigenvalue problem of Eq. (2.20), we break the rule of Eq. (2.18). As an example, let us assume that the translational symmetry of the nanostructure is along the $\vec{b}_3$ direction. The planar k-grid $\vec{k}_{\perp,\Gamma}$ is formed by setting $m_3 = 0$ and driven by $\vec{q}_{m_1,m_2,m_3} = \vec{b}_1 \frac{m_1}{N_1} + \vec{b}_2 \frac{m_2}{N_2} + \vec{k}_{\parallel}$ so that we do not need to increase N_3 . Then the separated eigenvalue problems of Eq. (2.20) are solved at definite $\vec{k}_{\parallel}$ values to obtain the energy dispersion $E(\vec{k}_{\parallel})$.

In regard to Hamiltonian matrix elements of Eq. (2.20), as we are solving the Schrödinger equation at a definite $\vec{k}_{\parallel}$, we have $\vec{k}_{\perp} = \vec{k}_{\parallel} + \vec{k}_{\perp,\Gamma}$ and $\vec{k}'_{\perp} = \vec{k}_{\parallel} + \vec{k}'_{\perp,\Gamma}$. Moreover, owing to the atomic periodicity of the NW along its axial direction, we can take $\vec{R}_l = \vec{R}_{l,\perp}$ so that the supercell can be scanned with the vector $\vec{r} = \vec{R}_{l,\perp} + \vec{r}_p$ where we recall that $\vec{r}_p$ is the position vector inside the primitive cell. Within this picture, the matrix elements $\langle n'\vec{k}'_{\perp}\vec{k}'_{\parallel}\sigma' | n\vec{k}_{\perp}\vec{k}_{\parallel}\sigma \rangle$ can be written as

$$\begin{aligned} \langle n'\vec{k}'_{\perp}\vec{k}'_{\parallel}\sigma' | n\vec{k}_{\perp}\vec{k}_{\parallel}\sigma \rangle &= \frac{1}{N_{\perp}} \int_V d^3r \frac{1}{\Omega_o} \sum_{\vec{G}',\vec{G}} B_{n'\vec{k}'_{\perp}}^{\sigma'}(\vec{G}')^* B_{n\vec{k}_{\perp}}^{\sigma}(\vec{G}) \\ &\quad \times e^{i(\vec{k}_{\perp}-\vec{k}'_{\perp}+\vec{G}_{\perp}-\vec{G}'_{\perp})\cdot\vec{r}_{\perp}} e^{i(k_{\parallel}-k'_{\parallel}+G_{\parallel}-G'_{\parallel})r_{\parallel}}. \end{aligned}$$

In the NW quantization model we have $\vec{r} = \vec{R}_{\perp,l} + \vec{r}_{\perp,p} + \vec{r}_{\parallel,p}$ so that $\vec{r}_{\perp} = \vec{R}_{\perp,l} + \vec{r}_{\perp,p}$ and $\vec{r}_{\parallel} = \vec{r}_{\parallel,p}$. Also using $\int_V d^3r \rightarrow \sum_{l=1}^{N_{\perp}} \int_{A_o} d^2r_{\perp,p} \int_{L_o} dr_{\parallel,p}$ and since we are at a definite $k_{\parallel} = k'_{\parallel}$, we can write $\langle n'\vec{k}'_{\perp}\vec{k}'_{\parallel}\sigma' | n\vec{k}_{\perp}\vec{k}_{\parallel}\sigma \rangle$ elements as

$$\begin{aligned} \langle n'\vec{k}'_{\perp}\vec{k}'_{\parallel}\sigma' | n\vec{k}_{\perp}\vec{k}_{\parallel}\sigma \rangle &= \sum_{\vec{G}',\vec{G}} B_{n'\vec{k}'_{\perp}}^{\sigma'}(\vec{G}')^* B_{n\vec{k}_{\perp}}^{\sigma}(\vec{G}) \frac{1}{N_{\perp}} \sum_{l=1}^{N_{\perp}} e^{i(\vec{k}_{\perp}-\vec{k}'_{\perp})\cdot\vec{R}_{\perp,l}} \\ &\quad \times \frac{1}{A_o} \int_{A_o} d^2r_{\perp,p} e^{i(\vec{G}_{\perp}-\vec{G}'_{\perp})\cdot\vec{r}_{\perp,p}} \frac{1}{L_o} \int_{L_o} dr_{\parallel,p} e^{i(G_{\parallel}-G'_{\parallel})r_{\parallel}} \\ &= \sum_{\vec{G}',\vec{G}} B_{n'\vec{k}'_{\perp}}^{\sigma'}(\vec{G}')^* B_{n\vec{k}_{\perp}}^{\sigma}(\vec{G}) \delta_{\vec{k}_{\perp},\vec{k}'_{\perp}} \delta_{\vec{G}_{\perp},\vec{G}'_{\perp}} \delta_{G_{\parallel},G'_{\parallel}} = \sum_{\vec{G}} B_{n'\vec{k}'_{\perp}}^{\sigma'}(\vec{G})^* B_{n\vec{k}_{\perp}}^{\sigma}(\vec{G}) \delta_{\vec{k}_{\perp},\vec{k}'_{\perp}}, \end{aligned} \tag{2.21}$$

where we exploit the identities that $e^{i(\vec{G}_\perp - \vec{G}'_\perp) \cdot \vec{R}_{\perp,l}} = 1$, $\frac{1}{N_\perp} \sum_{l=1}^{N_\perp} e^{i(\vec{k}_\perp - \vec{k}'_\perp) \cdot \vec{R}_{\perp,l}} = \delta_{\vec{k}_\perp, \vec{k}'_\perp}$, $\frac{1}{A_o} \int_{A_o} d^2 r_{\perp,p} e^{i(\vec{G}_\perp - \vec{G}'_\perp) \cdot \vec{r}_{\perp,p}} = \delta_{\vec{G}_\perp, \vec{G}'_\perp}$ and $\frac{1}{L_o} \int_{L_o} dr_{\parallel,p} e^{i(G_\parallel - G'_\parallel)r_\parallel} = \delta_{G_\parallel, G'_\parallel}$.

In regard to computational implementation, since we are solving the Schrödinger equation at a specific $\vec{k}_\parallel$, we already have an intrinsic $\delta_{\vec{k}_\parallel, \vec{k}'_\parallel}$ that again allows us to write $\delta_{\vec{k}_\perp, \vec{k}'_\perp} \rightarrow \delta_{\vec{k}, \vec{k}'}$. Hence, actually Eqs. 2.10 and 2.21 come up with the same form. That is similar for the kinetic and potential energy matrix elements. Therefore only giving a planar k-grid is enough to run the 3D k-grid based implementation for 2D k-grid case of 1D translational structures. Further discussion about the k-space construction and sampling is given in Sec. 2.3.

2.2 Oxide Passivation and Atomic Pseudopotentials

An important aspect of the electronic structure calculations is the surface passivation. The surface of an unpassivated nanostructure consists of dangling bonds which introduces surface states. These localized states lie in the otherwise forbidden band gap. Surface passivation removes these surface states. From the transport point of view, the passivated surface eliminates the carrier recombination centers and hence enhances the current flow. Actual grown Si NWs samples have passivated surfaces achieved usually either by oxidation or hydrogenation. The latter is rather simple to model computationally: Each Si dangling bond is terminated by forming a stable one layer Si-H binding. The representation of oxide passivation is more difficult, since a large number of atoms is need to describe the thick oxide layer [14]. For this reason, in the study of Si NWs, mostly H-passivation is used as a viable approximation to the oxide passivation [20, 50]. Without increasing the computational cost, instead of H some different materials are also employed to terminate the dangling bonds such as Br, Cl, I [51], OH, NH₂ [53, 52], and F [9]. However, due to the practical instabilities of these passivations, the calculations of oxide passivated Si NWs becomes essential. For the realistic oxide-passivation, a first principles study of amorphous oxide sheathed

Table 2.1: Parameters of the pseudopotential form factors [see Eq. (2.22)] of Si and the wide band-gap matrix which represents SiO₂. Units are given in the text.

	a_1	a_2	a_3	a_4	a_5	a_6
Si	106.0686	2.2278	0.606	-1.972	5.0	0.3
Matrix-Si	69.625	2.614	0.0786	-19.1433	5.99	0.335

thin Si NWs has been reported [129]. As reported in this work there can be subtle differences between the H- and oxide-passivations, such as in the band gap orderings of different orientation Si NWs.

In our implementation, the surface passivation is provided by embedding the NW structures into a host matrix, being usually silica. However, the EPM calculations for oxygen is quite troublesome and, yet more, the different lattice structure of SiO₂, with reference to Si, causes strain effects. To overcome these obstacles, we propose an *artificial* wide band gap material that computationally substitutes silica. In detail, after constructing the Si NW core, all the remaining crystal points within the computational supercell are filled with the *artificial oxide atoms*. This artificial embedding material has the same dielectric constant of SiO₂ and band edge lineup, with respect to Si, however with the diamond structure to prevent complications associated with strain [123].

For the local empirical pseudopotentials of Si and SiO₂, we use the functional form introduced by Freidel *et al.* [130] These authors suggest an analytical expression to produce the pseudopotential form factor at a given general wave number q

$$V_{PP}(q) = \frac{a_1(q^2 - a_2)}{e^{a_3(q^2 - a_4)} + 1} \left[\frac{1}{2} \tanh \left(\frac{a_5 - q^2}{a_6} \right) + \frac{1}{2} \right]. \quad (2.22)$$

We employ their parameters for Si (listed in Table 2.1) [130]. On the other hand, we have generated *new* pseudopotential parameters for the artificial SiO₂ which reproduces the experimental band alignments of bulk Si/SiO₂ interface as 4.4 eV and 3.4 eV for the valence [131] and conduction [132] band edges, respectively. The parameter generation is performed via the simulated annealing

optimization method [133, 134] starting from those of bulk Si. The corresponding parameters are given in Table 2.1. The units are arranged such that the pseudopotential form factors come out in Rydbergs and the wave number q in Eq.(2.22) should be in the atomic units (1/Bohr radius). For the plane-wave cut-off energies of EPM, we use 14 Ry for both Si and artificial SiO₂. The resultant bulk band structures for Si and artificial oxide matrix are plotted in Fig. 2.1. To give a comparison DFT-produced band structure of bulk Si is also given in Fig. 2.1. The band gap of the latter is set equal to EPM band gap by a scissor operation.

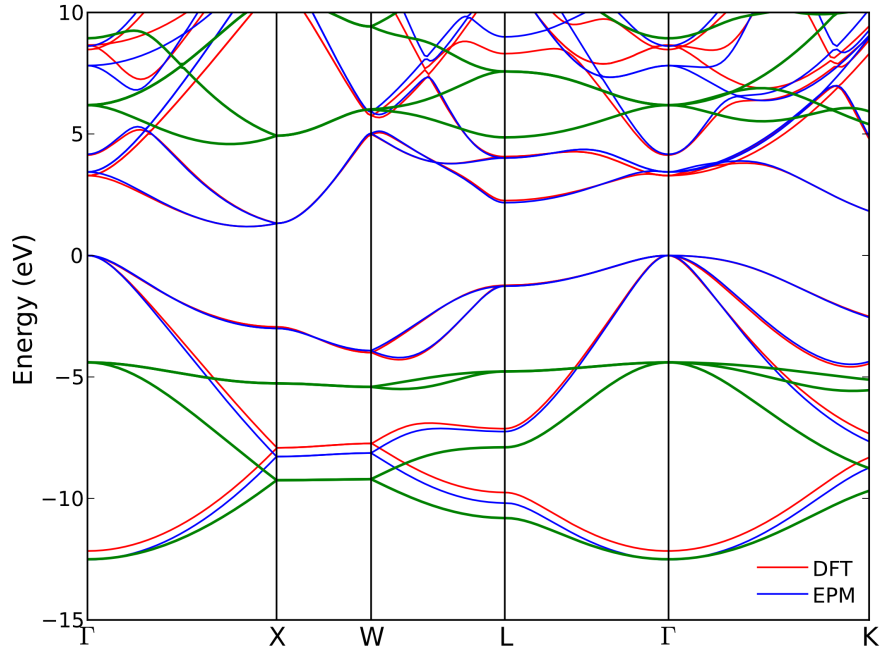


Figure 2.1: EPM band structures for bulk Si (blue) and artificial wide band gap matrix (green) together with DFT bandstructure of Si (red) with band gap error corrected.

We note that in our oxide passivation approach, there is an arbitrariness on the pseudopotential representation of the wide band gap material. To overcome this arbitrariness, we checked the oxide passivation with different pseudopotentials, all satisfying the same Si/SiO₂ interface. We observed that although the calculated band gap values might vary slightly, the electronic energy and transport characteristics that we discuss in the following chapters are robust.

Though the surface chemistry of oxide-passivation requires more elaborate first principles calculations, considering today’s DFT computation limits, we believe that our approach offers a viable alternative for the calculations of oxide-embedded large scale Si nanostructures.

Despite the missing surface relaxation and strain effects, the reliability and competence of our computation method has gained confidence, in the context of embedded Si and Ge nanocrystals, comparing with experimental data for the linear [123] and third-order nonlinear optical properties [124, 135], the quantum-confined Stark effect [126] as well as for the Auger recombination and carrier multiplication [125].

2.2.1 Filtering of oxide-derived surface states

Strictly speaking, the “good” artificial oxide is generated with the intension to remove all surface states which lie in the otherwise forbidden band gap. We observed that the oxide matrix can meet this purpose unless the matrix Bloch functions $B_{n\vec{k}}^{SiO_2}$ are included into the expansion basis of LCBB [see Eq.(2.5)]. Note that even when we do not include the matrix Bloch functions into the expansion basis, the system Hamiltonian still “knows” the existence of oxide medium thanks to the weight functions and pseudopotential terms [referring to Eq. (2.6)].

Fig. 2.2 shows the calculated energy spectra for an embedded silicon nanocrystal of diameter of 1.6 nm for the case that the oxide Bloch functions $B_{n\vec{k}}^{SiO_2}$ are included to the LCBB expansion basis. In this part we consider nanocrystals, as surface-to-volume ratio is larger in comparison to NWs, the surface effects are more dominant. Although the band gap is consistent with the result of other electronic structure methods and experiment [123], there is a subtle problem here. As we look for the density of states, we notice that there is a premature oxide continuum in valence band (VB) energies at about -2.5 eV. From our SiO₂ matrix generation, we know that the VB edge of SiO₂ matrix should be around -5.4 eV.¹

¹In our calculations bulk Si band-edges are at energies about -0.97 eV and 0.21 eV for VB

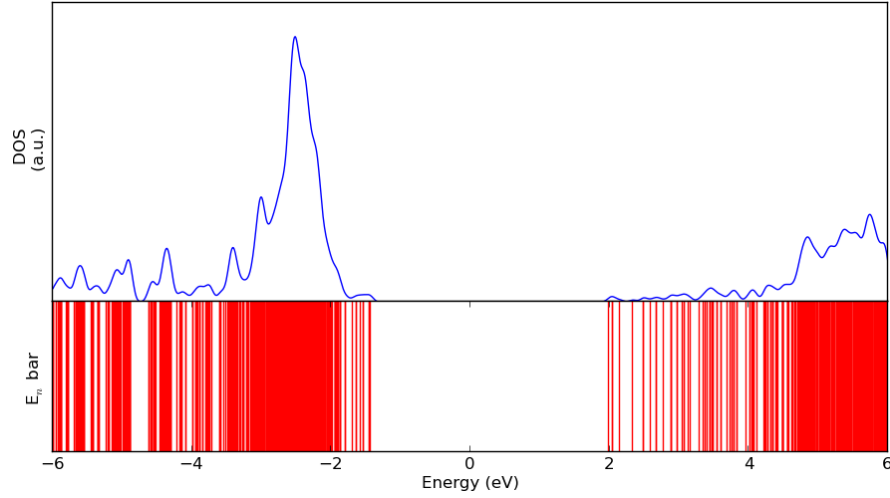


Figure 2.2: The energy spectrum of an embedded silicon nanocrystal of diameter of 1.6 nm for the case where the oxide Bloch functions are not included to the LCBB expansion basis. The corresponding Gaussian broadened density of states is given with broadening parameter of 0.05 eV. The band-edges and the gap can be clearly seen.

To correct this premature band edge, we include the matrix Bloch functions into the LCBB expansion basis. The cost of this inclusion is that the computational load increases linearly with the increasing basis size [115]. Fig. 2.3 shows the resulting energy spectrum. Now the oxide continua seem to be at their proper place. Nevertheless, we have another problem that the forbidden band gap of the nanocrystal has been contaminated with the surface states. To extract the band gap back, we need to filter the calculated energy states. Hence, the computational load increases further due to the filtering requirements. One immediate way of performing energy state filtration is to plot the carrier charge densities (as square modulus of wave functions) and then sift through them. Fig. 2.4 indicates two representative cases: (a) an electronic state derived from the core of the nanocrystal so that localizes therein, whereas (b) a state derived from the oxide matrix which spreads through the matrix and localizes therein. This approach seems effective, however, it requires high computational load (and human perception) due to the construction of wave functions in the real space.

and CB edges, respectively. These values are -5.4 eV and 3.6 eV for the SiO₂ matrix in order that it has a band gap of 9 eV and satisfies the proper band alignments of Si/SiO₂ interface as described in Sec. 2.2.

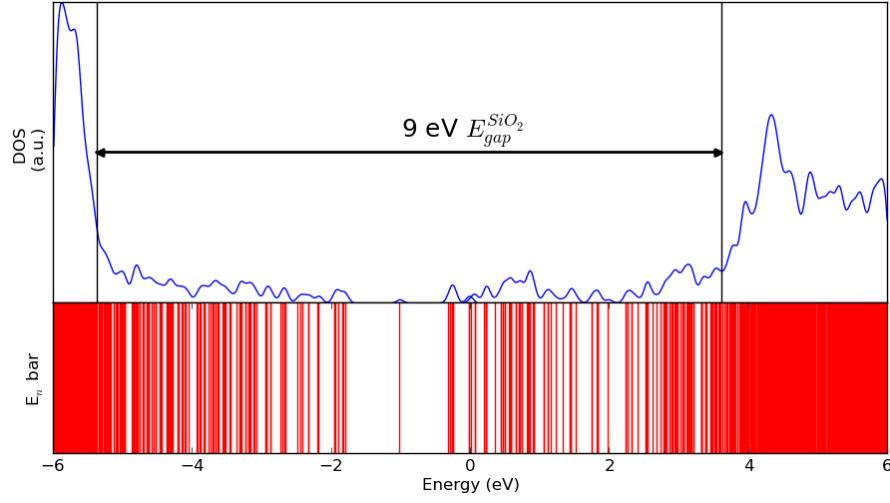


Figure 2.3: The energy spectrum and the corresponding density of states of the embedded nanocrystal of diameter of 1.6 nm with the oxide Bloch functions included to the LCBB expansion basis. The band-edges get lost due to the surface states as well as the band gap.

Thus, we aim to introduce an automatic and fast filtering procedure. Our tests and observations shows that this filtering can be done properly by exploiting the LCBB expansion coefficients, i.e., $C_{n,\vec{k},j}^\sigma$ terms, such that if for a specific state the core and matrix expansion coefficients satisfy the condition that

$$\sum_{n,\vec{k}} \left| C_{n,\vec{k},j}^{\text{SiO}_2} \right|^2 \leq \mathcal{F} \cdot \sum_{n,\vec{k}} \left| C_{n,\vec{k},j}^{\text{Si}} \right|^2, \quad (2.23)$$

this state is a core-derived state and should be retained. Here, $\mathcal{F}$ is the filtering parameter, being taken as 0.4 all through the calculations of this work.

Fig. 2.5 shows the filtered version of Fig. 2.3. As seen in the figure, the proper band gap is restored. Notably, both VB and CB edges shifted slightly with respect to the matrix-Bloch-functions-*not*-included case, yet the shifts are such that the band gap value is not affected.

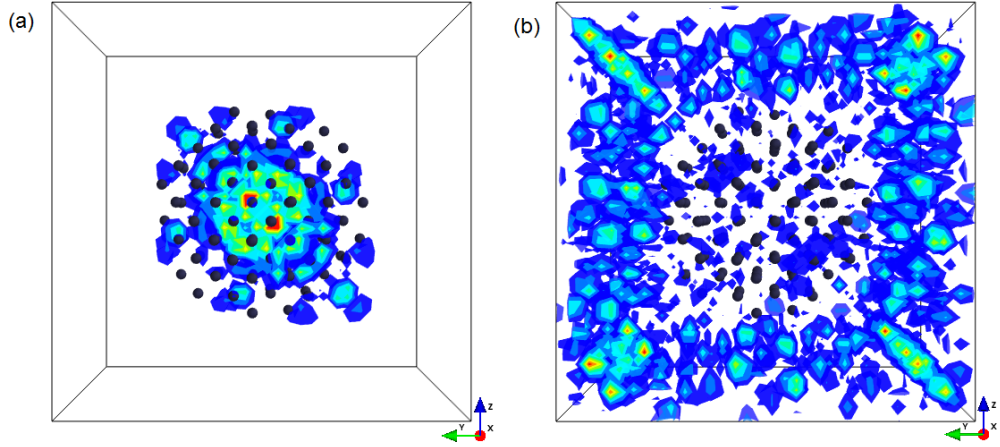


Figure 2.4: Isosurfaces of charge densities for two representative states of the embedded nanocrystal of Fig. 2.3. (a) The core-derived state of nanocrystal, (b) the oxide matrix-derived state. The isosurfaces enclose densities from the respective maximum to 10% of that. The black points represent the core Si atoms.

2.3 Construction of the Expansion Basis

Considering Eq. (2.5), the LCBB basis set construction has two aspects: (i) the number of bulk bands included to the LCBB expansion [band indices n in Eq. (2.5)], (ii) k-point selection to sample the bulk BZ [wave vector $\vec{k}$ in Eq. (2.5)].

In regard to number of bulk bands, we include three highest bulk VBs and four lowest CBs of both Si and silica into the expansion basis. The results of Ch. 3 are obtained within this construction. For the transport calculations of Ch. 5, for the conduction states, we include only the two lowest bulk CBs of Si and none for the silica to deal with cleaner dispersion, i.e., less surface states and less filtering effort. We verified that this two CB consideration gives the same band structure at the band edges with the former four CB basis. We tested and observed that further increase in the number of bulk bands does not change the band edge energies, whereas the deeper states beyond the band edges are affected. In this work, we keep our analysis always in the energy windows very close to band edges (~ 0.5 to 1 eV below/above the VB maximum/CB minimum) and we mainly focus on the trends rather than the “exact” energy values of

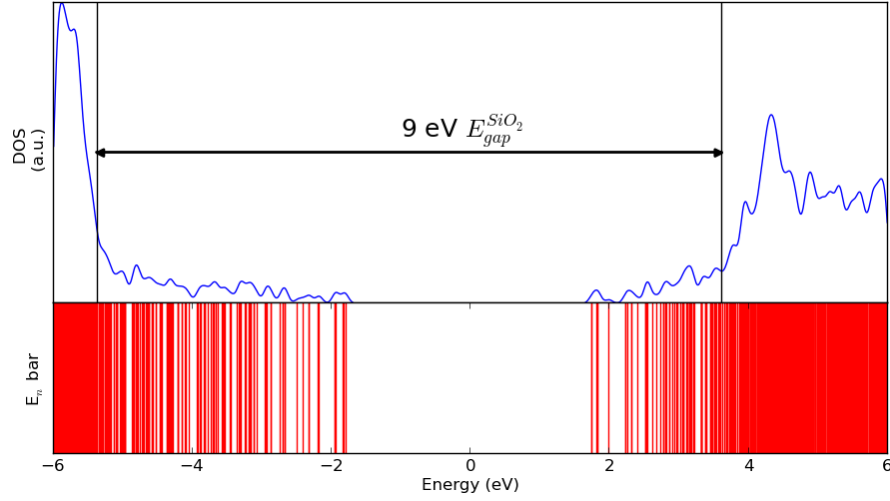


Figure 2.5: Same as Fig. 2.3 but now the energy states are filtered with the expression given in Eq. (2.23). After the filtering, the band-edges have become visible and the band gap is restored.

nanostructures. Accordingly, those included bulk bands meet the concerns of this work.

As another technical issue, k-point selection is very critical for the performance of LCB method. We build up the nanostructures employing either a two-atom or an eight-atom Si basis. Hence, the underlying Bravais lattice is either face-centered cubic (fcc) or simple cubic (sc) lattice, respectively. A real space fcc lattice has body-centered cubic (bcc) reciprocal lattice whereas the two space are of the same lattice structure for the sc case. We sample the k-points from a volume enclosed by the planes which are perpendicular bisectors of the reciprocal lattice primitive vectors centered around the Γ [136]. The volume has a parallelepiped shape (not the conventional orthorhombic BZ) for the two-atom basis (fcc case) and the cubic shape for the eight-atom basis (sc case).

In 3D k-space implementation of LCB, we form a 3D mesh of k-points within the corresponding volume. In the case of 2D k-space implementation, however, we form a planar k-grid at Γ , $\vec{k}_{\perp,\Gamma}$ —corresponds to one of the 2D grids out of the 3D mesh (illustrated in Fig. 2.6)—satisfying that the plane is perpendicular to the energy dispersion direction. Then for each separated eigenvalue problem

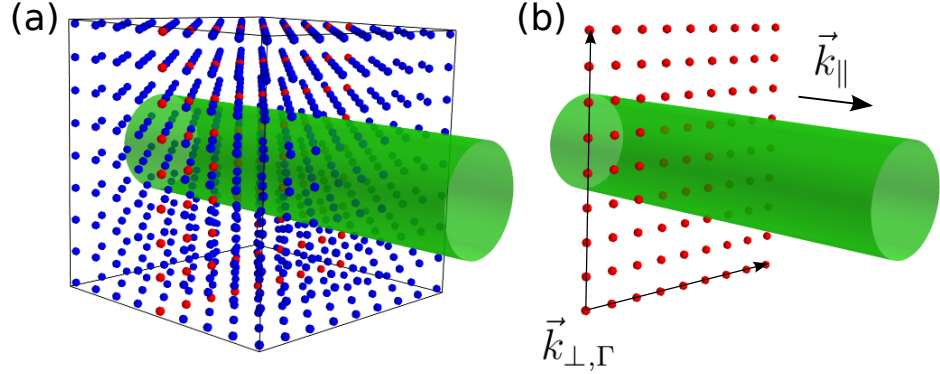


Figure 2.6: Schematic illustration of (a) 3D and (b) 2D k-grids. The tube indicates the alignment of NW. To solve the separated eigenvalue problems of Eq. (2.20), the planar k-grid $\vec{k}_{\perp, \Gamma}$ formed at Γ (red grid points in the figure) is shifted along the dispersion direction by $\vec{k}_{\perp} = \vec{k}_{\perp, \Gamma} + \vec{k}_{\parallel}$.

of Eq. (2.20), this planar k-grid is shifted by $\vec{k}_{\perp} = \vec{k}_{\perp, \Gamma} + \vec{k}_{\parallel}$ along the dispersion direction to compute the energy dispersion $E(\vec{k}_{\parallel})$ at definite $\vec{k}_{\parallel}$ values.

2.3.1 Convergence Performance of Band Edges

As a final remark about the expansion basis, we analyze the convergences of valence band edge (VBE) and conduction band edge (CBE) with respect to k-point sampling. The convergence tests are conducted in two parts: (i) the number of k-points in $\vec{k}_{\perp}$ plane [shown in Fig. 2.7 (a) setting number of $\vec{k}_{\parallel}$ points as 100], (ii) the number of $\vec{k}_{\parallel}$ points along the 1D BZ of a NW [shown in Fig. 2.7 (b) setting number of $\vec{k}_{\perp}$ points as 13×13]. We note that $\vec{k}_{\parallel}$ is scanning *half* zone, i.e., from Brillouin zone center Γ to zone boundary Z , not the full zone $-ZZ$. However, the planar k-grid $\vec{k}_{\perp}$ samples the full zone $-ZZ$ in both perpendicular directions. In other words, say 7 of Fig. 2.7 (b) corresponds to the number 13 of Fig. 2.7 (a).

The convergence performances are shown in Fig. 2.7 for a representative nanostructure of $\langle 110 \rangle$ -oriented Si NW of diameter of 2 nm. In this part, we consider only the band edge convergences. We discuss the band dispersion convergence in

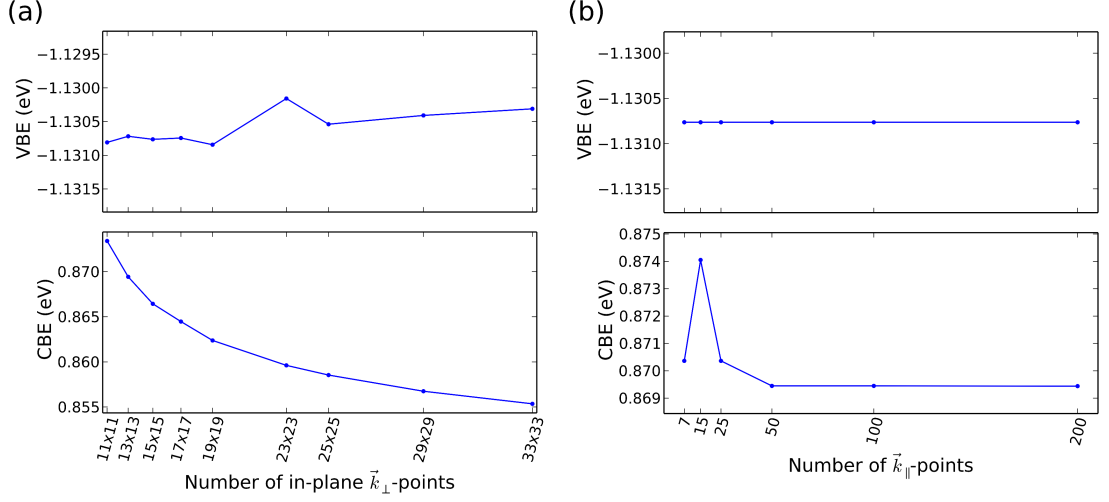


Figure 2.7: Convergence of valence (VBE) and conduction (CBE) band edges as a function of number of (a) in plane $\vec{k}_\perp$ -points (setting number of $\vec{k}_\parallel$ points as 100) and (b) $\vec{k}_\parallel$ -points from Γ to zone boundary Z (setting number of $\vec{k}_\perp$ -grid as 13×13). Notice that the energy scales are different.

Ch. 4, in conjunction with the transport calculations.

Bulk Si has the VBE at the Γ -point and the six CBEs are located around $0.85\Gamma X$, i.e., around $1.7 \frac{\pi}{a_{Si}}$ along the $\langle 100 \rangle$ directions, where a_{Si} is the lattice constant of bulk Si. The bulk band structure manifests itself in the convergence tests. The VBE of the NW converges very rapidly (even to less than 1 meV) for the given number of k-points on the plots, since the k-grid is already centered at Γ -point and sampled around it. By the same gridding actually, the CBE convergence is slower. Still, beyond a $\vec{k}_\perp$ -gridding of size 15×15 , the further change of the CBE reduces below 10 meV. These two figures together also represents the convergence performance of 3D k-gridding. As long as the number of k-points is $15 \times 15 \times 15$ or larger, the band edge energies are converged with respect to the number of k-points, to within ~ 10 meV.

The convergence criterion is very similar for the different size and shape nanostructures. Let us explain this general comment. Once we construct a nanostructure within a computational supercell, we have a *minimum* size for the supercell

which is obviously determined by the shape and size of the nanostructure considered—we also include an additional passivation medium to the supercell to eliminate the possible inter-supercell (periodic image) interactions. Thus, the N_i numbers given in Eq. (2.17) have lower limits. Then Eq. (2.18) dictates the corresponding *minimum* values of k-grid. For example, for the NW considered in Fig. 2.7, the minimum k-gridding numbers are $11 \times 11 \times 1$ (since the NW has a translational symmetry along its axis the last number is trivial). To sum up, the convergence criterion is very similar starting from these *minimum* numbers the convergence is very quick as shown in Fig. 2.7. For all the calculations given in this work, first, the convergence is tested and ensured.

For the calculations of Ch. 3, we employ 3D k-gridding for both single NWs and NW networks. Although the single NW calculations can also be performed with the 2D k-gridding, we keep 3D k-space to investigate both the NWs and NW networks with the same resolution of k-gridding. Nevertheless, for the transport calculations of Ch. 5, as our analysis given in Ch. 4 indicates, denser resolution of energy dispersion along the NW direction is a must to obtain the proper conduction steps. Henceforth, in the transport calculations of NWs, we employ the planar 2D k-grid approach.

2.4 Computational Budget of Our Implementation

Our in-house LCBB code is written in Fortran employing the modern aspects of the language. Parallelizations are done using openMP with the Intel Fortran compiler [137]. In our computations, the time and memory budget is related with the size of the expansion basis as well as the number of atoms in the supercell. The electronic structure computation involves five main steps with a number of sub-tasks:

Forming expansion basis sets -(S1) After generating the computational supercell, which hosts the nanostructure, the LCBB expansion basis is formed.

This step comprises the k-grid allocation and solution of bulk EPM Hamiltonian in order to obtain the B_{nk}^σ coefficients for the formation of corresponding LCBB expansion basis [see Eq. (2.5)]. Regarding the time consumption, S1 takes about several minutes even for the largest systems considered in this work. The reduced computational demand of EPM has a great contribution on that.

Forming Fourier transform tables - (S2) Before starting to deal with the LCBB Hamiltonian, the required Fourier transforms are tabulated storing the matrix elements defined in Eqs. (2.15) and (2.16). We employ discrete Fourier transform (DFT) in our calculations. We note that N -point DFT scales with N^2 here N is directly proportional to the number of primitive cells in the supercell and also scales with the k-grid, whereas the fast Fourier transform (FFT) scales with $(N/2) \log_2 N$ [138, 134]. Thus, the FFT provides a computational efficiency by a factor of over 200 even when the basis size is about 1000. It must be noted that FFT requires an equally-spaced uniform real space lattice. However, in the case of *strained* nanostructures this is not the case where atoms are on a locally deformed grid. One can still try to use FFT using Taylor series expansions around the undeformed grid (see for instance [114]), but this introduces yet another layer of approximation. For this reason, we prefer to stay with exact formulation based on DFT and deal with its excessive budget using off-line tabulation as mentioned below.

The computations of this work are performed mainly in two machines: (M1) a quad-core Intel Core i3-2120 CPU of 3.30 GHz with 4 GB RAM desktop machine and (M2) 24-core Intel Xeon E7530 CPU of 1.87 GHz with 96 GB RAM server machine. For a representative calculation, for instance, M1 performs the DFT tabulating in 3 hours, whereas in M2, the same steps takes more than 20 hours, both running the same parallelized code, same version of the Intel Fortran compilers. This indicates that the CPU speed is more important than the number of CPUs. Higher parallelization has a negative effect on this step. In that manner, the hyper threading has a worse effect on the computation time. On the other hand M1 cannot handle the rest of the computation because of its limited RAM. As a solution to the bottleneck for demanding computations, we have tabulated the DFT elements in M1, and the rest of the computation is performed on M2.

Hamiltonian matrix filling -(S3) and **Eigenvector solver** -(S4) This is followed by the filling and solving of the LCBB Hamiltonian. For an expansion basis set of N elements, the Hamiltonian filling is scaling with N^2 , whereas the solution of generalized matrix scales with N^3 , this directly reflect to time consumption. For this step considering both the memory and parallelization capabilities, M2 has a great superiority on M1.

Postprocessing -(S5) The last step is the post-electronic structure process, also including the matrix-derived state filtering. Once the electronic structure is obtained, further physical quantities such as momentum matrix elements, absorption coefficients, relaxation times, to name a few, can be calculated. This is the final step in our treatment. This step is relatively fast if the computations are done in the k-space, i.e. via $C_{n,\vec{k},j}^\sigma$ coefficients. In Ch. 5, we consider real-space wave functions to generate charge densities where the calculations take longer time such as for a system of basis size of about 20000 elements, consuming about half an hour per state and scales linearly with the expansion basis size.

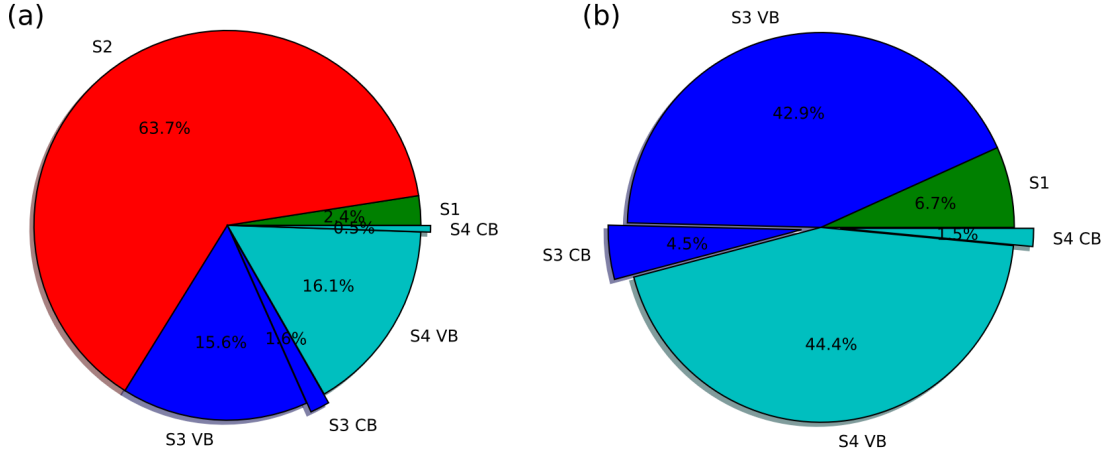


Figure 2.8: (a) Time sharing of our computational implementation. Total wall-time of the representative computation is 12.3 hours. (b) Step S2 is done on the machine M1 off-line. The successive steps are described in the text.

All the time consuming computation steps are parallelized. To give a rough sense of total computation time, in Fig.2.8(a), we present the time sharing of aforementioned steps for a representative computation: the supercell contains

5488 atoms, the LCBB basis is constructed with 6 bulk VBs (3 core + 3 oxide), and 2 core bulk CBs. Considering a 3D k-grid of $15 \times 15 \times 15$ sampling points, the LCBB basis contains in total $(6+2) \times (15 \times 15 \times 15) = 27000$ elements. Excluding S5, the total computation time is 12.3 hours on M2. As seen on the figure, S2 takes more than half of the time. Performing S2 on M1 off-line, the total computation time gets halved. Then the time partitioning alters to form as shown in Fig.2.8(b). In the figures, we have separated CB and VB times to indicate the scaling with the number of bulk bands.

Further discussions about the computational considerations of LCBB method such as matrix element evaluation, diagonalization of Hamiltonian, and plane wave smooth cutoff function can be found in the original works [114, 115].

Chapter 3

Electronic Structure of Si Nanowires and Nanowire Networks

As we review in Ch. 1, the electronic structure of Si NWs have been extensively studied in the last two decades. Accordingly, the *research* of single Si NWs has by and large lost its novelty. Nevertheless, the *reanalysis* of well-established single Si NWs case gives us an opportunity to test the reliability of our electronic structure calculation method before entering the obscure field of Si NW networks (NWNs). More importantly, to comprehend the physical properties of NWNs, first, a solid understanding of single NW is fundamental.

For this purpose, in this chapter, first, in Sec. 3.1 we consider single Si NWs aligned in different crystalline directions. We report the calculated band gaps as well as band edge alignments with respect to those of bulk Si. The details of the band structures are discussed in Sec. 3.1.1 in the light of effective mass theory and Brillouin zone foldings. This is followed in Sec. 3.2 by the detailed analysis of Si NWNs. Comprehensive band gap data of NWNs is consolidated into a general expression which supports an efficient way to estimate the band gaps of Si NWNs. In the last part of this chapter, considering the device applications, we provide

the band-offsets of Si NWs and NWNs with respect to the band edges of bulk Si and SiO₂.

3.1 Results on Si Nanowires

To pave the way to NWNs, first, we investigate the oxide-embedded Si NWs oriented along the $\langle 100 \rangle$, $\langle 110 \rangle$, $\langle 111 \rangle$, and $\langle 112 \rangle$ crystalline directions. Since the band gap is rather insensitive to the cross-section shape as long as the mean diameter is the same [9], we carve out essentially cylindrically shaped NWs out of the bulk Si, and embed them into the oxide to passivate the dangling bonds. The resulting NWs are one-dimensional periodic structures. For different NW orientations, depending on bulk Si crystalline symmetries, NW unit cell length a_{wire} has different values such that $a_{\langle 100 \rangle} = a_{Si}$, $a_{\langle 110 \rangle} = a_{Si}/\sqrt{2}$, $a_{\langle 111 \rangle} = a_{Si}\sqrt{3}$, and $a_{\langle 112 \rangle} = a_{Si}\sqrt{6}/2$, where a_{Si} is the bulk Si lattice constant. We define the mean NW diameter as the diameter of the cylinder of length a_{wire} whose volume is the same as the average volume $\Omega = N_{Si}a^3/8$ occupied by the N_{Si} number of Si atoms in the NW unit cell [139]. Within our embedding into oxide framework such a definition of diameter is more proper than taking the twice of the average distance of terminating atoms from the NW center [5]. In our calculations, NW diameters range from 1 to 10 nm for different directions. We report the effective electronic band gaps, without discriminating between their direct or indirect gap characters. This is in accordance with the purpose of this work, which aims to shed light on how energy gaps are inherited from wires to networks.

A supercell approach is employed while constructing the NW structures and the supercell is repeated in all three-dimensions. The supercell sizes are set large enough to prevent the interaction between the structures and their images in neighboring cells (at least 2 nm distance from surface to surface for single NWs and inter-junction separation for NWNs). Spin-orbit coupling is not taken into account in the calculations to reduce the computation time, relying on our representative calculations that it only affects the band gap energies in the meV range.

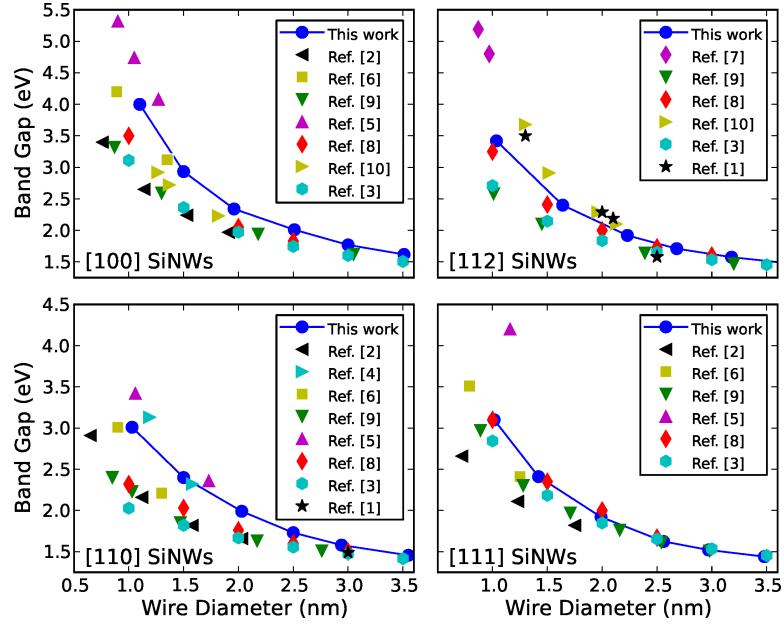


Figure 3.1: Band gap energies as a function of diameter for [100], [112], [110], and [111]-oriented Si NWs. Our results for oxide-passivated NWs (solid lines with filled circles) are compared with data of experimental [1] and theoretical results of H-passivated NWs including empirical pseudopotential method [2], semiempirical tight binding [3], and DFT calculations correcting band gaps with GW approximation [4, 5, 6, 7], hybrid functionals [8, 9], or scissors operation [10]. (Reproduced with permission from Ref. [11]. Copyright 2013, AIP Publishing LLC.)

In Fig. 3.1, our results are reported and compared with a compilation of some representative experimental and theoretical results for NW diameters in the range 0.5 nm to 3.5 nm. Note that our results are for Si NWs embedded into oxide whereas all the other results are for H-passivated Si NWs. In general terms, our passivation scheme is observed to show similar trends with that of H-passivation, however, the large spread over data of latter renders a more specific comparison difficult. Still, the figure demonstrates that our results yield remarkable agreement with the published band gap energies and thus verify the reliability of our scheme.

The experimental detection of electronic structure is very challenging. The only experimental data on the *electronic* band gaps of Si NWs comes from Ref. [1] in which the band gaps are measured by scanning tunneling spectroscopy (STS).

As seen on the figure, most of the theoretical works underestimates the STS band gaps. As the authors mention [1], this maybe due to the overestimation of NW diameters in scanning tunneling microscopy measurements. This is consistent with the fact that the only theoretical result which succeeds to catch the experiment data introduces effective diameters in the calculations by considering the penetration of wave functions in to the vacuum.

The photoluminescence experiments give the optical band gaps. In Si NWs, due to excitonic effects, the *optical* band gaps are lower than the *electronic* band gaps in general [6]. The excitonic effects are beyond the scope of this single-particle work.

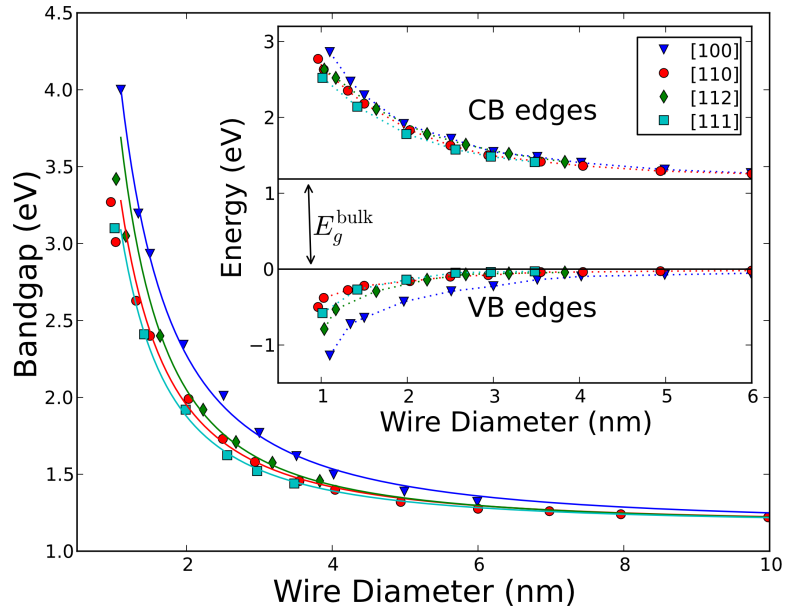


Figure 3.2: Band gap energy of oxide-passivated Si NWs as a function of diameter. The values are fitted with a $Cd^{-\alpha}$ form. Inset shows the variation of valence and conduction band edges. The dashed lines of the inset are just guides to the eyes. (Reproduced with permission from Ref. [11]. Copyright 2013, AIP Publishing LLC.)

To gain more insight into the orientation and size dependence, in Fig. 3.2, we plot our electronic band gap results for different NW orientations. In general, the gaps decrease asymptotically towards the bulk Si value with increasing NW diameter, reflecting the recession of the quantum size effect. In the figure, the

dependence of the band gap E_g on the wire diameter is described by

$$E_g = E_g^{\text{bulk}} + Cd^{-\alpha}, \quad (3.1)$$

as proposed according to the effective mass approximation [23]. In this expression, $E_g^{\text{bulk}} = 1.17 \text{ eV}$ is the experimental bulk band gap value, d is the diameter of the wire (in nm), and C and α are fitting parameters. The NW orientation dependent values of $\{C, \alpha\}$ parameters are listed in Table 3.1. Since the orientation dependence of band gaps is negligible beyond certain sizes (see Fig. 3.2; for $\langle 100 \rangle$ above 6 nm diameter, and for $\langle 111 \rangle$ and $\langle 112 \rangle$ above 3.5 nm), at those diameters, we employ the data of $\langle 110 \rangle$ NWs also for the fittings of the other directions.

The effective mass approximation (EMA) predicts a $1/d^2$ scaling for the single-particle state energies and thus for the band gaps, as the hallmark of the quantum size effect [140]. The quadratic behavior derives from the assumptions of an infinite potential barrier at the surface, parabolic bands and single-band framework. However, realistic NWs have a finite-potential wall which will allow penetration of wave functions into the passivation medium [10]. Moreover, the bands interact with each other so that the band edges are pushed towards the bulk edges, also leading to the breakdown of the EMA [141]. As shown in Ref. [141], EMA overestimates the band gaps below 4 nm diameters. Our calculations similarly reveal that the exponent significantly deviates from the quadratic scaling to values in the range 1.57 to 1.76 depending on the NW alignment (Table 3.1). *The disagreement with the EMA points out that atomistic treatment is required in the small size nanomaterials where the detailed structure becomes crucial.*

In the inset of Fig. 3.2, we point out the variation of valence band (VB) and conduction band (CB) edges as a function of NW diameter for different NW alignments. Indicating the band edges of the latter with horizontal solid lines, significantly, the figure also exemplifies the band edge alignments of Si NWs in regard to bulk Si for varying diameters. We disclose that the band edge energies obey the same size dependence just like the band gaps [see Eq. (3.1)]. Hence, the NW band edge energies can be described by $E_{\text{VBE}} = C_{\text{VBE}}d^{-\alpha_{\text{VBE}}}$ and $E_{\text{CBE}} = E_g^{\text{bulk}} + C_{\text{CBE}}d^{-\alpha_{\text{CBE}}}$, where $\{C_{\text{VBE}}, \alpha_{\text{VBE}}\}$ and $\{C_{\text{CBE}}, \alpha_{\text{CBE}}\}$ are fitting parameters (listed in Table 3.1), basing on the data points given in the inset of

Fig. 3.2. We note that α_{CBE} values are very close to the band gap exponents α , both being relatively less sensitive to NW alignment. In contrast, α_{VBE} has a dual character: $\langle 111 \rangle$ and $\langle 112 \rangle$ NW have values very close to 2, but $\langle 100 \rangle$ and $\langle 110 \rangle$ NWs significantly deviate from the $1/d^2$ character.

Table 3.1: Wire orientation-dependent fitting parameters associated with Eq. (3.1) (also used for Eq. (3.2)) for the main gap energy (C, α) as well as for VB ($C_{\text{VBE}}, \alpha_{\text{VBE}}$) and CB ($C_{\text{CBE}}, \alpha_{\text{CBE}}$) edge energies. When diameters d in Eqs. (3.1) and (3.2) are in nm units, the energies come out in units of eV.

	$\langle 100 \rangle$	$\langle 110 \rangle$	$\langle 111 \rangle$	$\langle 112 \rangle$
C	3.31	2.47	2.25	2.98
α	1.57	1.66	1.67	1.76
C_{VBE}	-1.22	-0.45	-0.49	-0.69
α_{VBE}	1.64	1.66	1.94	1.98
C_{CBE}	2.11	2.07	1.74	2.25
α_{CBE}	1.63	1.75	1.66	1.74

The theoretical works on H-passivated Si NWs reveals that the band gaps, E_g follows the orientation-dependent ordering $E_g^{\langle 100 \rangle} > E_g^{\langle 112 \rangle} \sim E_g^{\langle 111 \rangle} > E_g^{\langle 110 \rangle}$, up to diameters around 3 nm [9, 14]. In our oxide-passivation case, however, the ordering modifies to $E_g^{\langle 100 \rangle} > E_g^{\langle 112 \rangle} > E_g^{\langle 110 \rangle} \sim E_g^{\langle 111 \rangle}$. We have tested and observed that this ordering is robust under several different pseudopotential parameterizations of oxide matrix.

In the inset of Fig. 3.2, it can be seen that CB edge energies depend much more strongly on the wire diameter than VB edge energies. Such a behavior was theoretically predicted [123] and experimentally verified [142] for oxide embedded Si nanocrystals. Works of Refs. [3] and [5] present the VB and CB edges for H-passivated Si NWs which display similar trends as our band edge results. Nevertheless, for the $\langle 110 \rangle$ NWs they report a smaller variation for CB edge with diameter (even less than 0.5 eV), while in our case, the CB edge of $\langle 110 \rangle$ NWs changes as much as the edges of other directions. Hence, the distinct band gap ordering of oxide-passivated SiNWs in regard to H-passivated ones originates from the CB edges of $\langle 110 \rangle$ NWs. To shed light on this point, we can shortly review the band structure formation in Si NWs.

3.1.1 Band Structures of Si Nanowires

Bulk Si has an indirect band gap with six symmetric conduction band minima located around $\pm 0.85\Gamma X$, i.e. around $\pm 1.7\frac{\pi}{a}$ along $\langle 100 \rangle$ directions (illustrated in Fig. 3.3 (a)) and the valence band maximum is at the Γ -point. The ellipsoidal energy isosurfaces around these minima reflect that at those points the electrons have heavy longitudinal mass $m_l^* = 0.92 m_o$ and light transverse mass $m_t^* = 0.19 m_o$, m_o being the free electron mass. As the diameter of NW is reduced, the confinement effect modifies the band structure with orientation-dependent band foldings. In hindsight of the rest of this work, we focus on the $\langle 100 \rangle$ - and $\langle 110 \rangle$ -aligned Si NWs. The band folding discussions of $\langle 111 \rangle$ - and $\langle 112 \rangle$ -aligned NWs are similar and can be found in Refs. [3, 10].

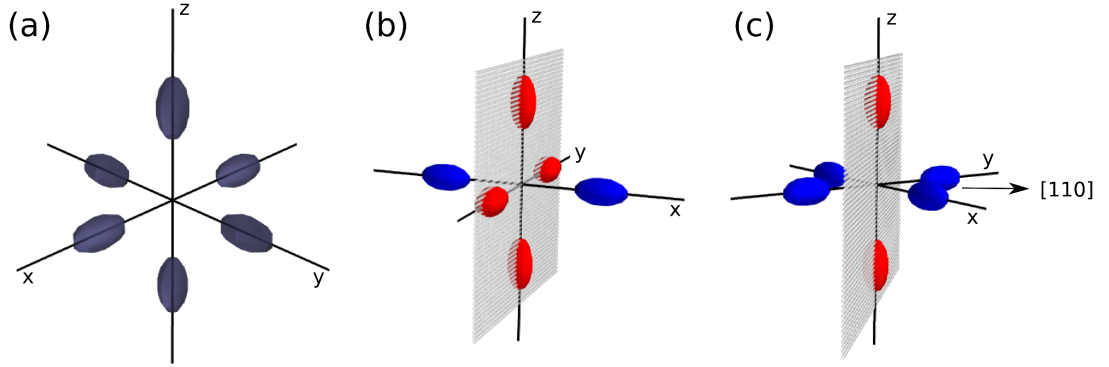


Figure 3.3: (a) Bulk Si has six equivalent ellipsoidal energy surfaces around the conduction band minima. The ellipsoids are described by the heavy longitudinal $m_l^* = 0.92 m_o$ and light transverse $m_t^* = 0.19 m_o$ masses. (b) For $\langle 100 \rangle$ -aligned Si NWs four of the six minima stay on the confinement plane and project to Γ -point. (c) For $\langle 110 \rangle$ -aligned Si NWs two of the six ones stay on the confinement plane and project to Γ . Those projecting to Γ -point are shown with red whereas the blue ones fold through the NW axial direction.

Regarding $\langle 100 \rangle$ -aligned Si NWs, the perpendicular confinement plane contains four of the six minima and those project onto Γ -point with effective mass $m^* = 0.19 m_o$. These are the minima along $\pm y$ and $\pm z$ (in Fig. 3.3 (b) shown by red ellipsoids). The remaining two minima of $\pm x$ project onto $k = \pm 1.7\frac{\pi}{a}$ with $m^* = 0.92 m_o$ (blue ones in the figure). Since for $\langle 100 \rangle$ -NWs, $a_{wire} = a_{Si}$

and using the fact that k -points have a periodicity of $\frac{2\pi}{a_{wire}}$, we can rewrite the projection point as $k = \pm 0.3 \frac{\pi}{a_{wire}}$.

For $\langle 110 \rangle$ -aligned Si NWs, the confinement plane contains two of the six conduction-band minima, folding with the effective mass $m^* = 0.19 m_o$ to Γ -point (demonstrated in Fig. 3.3(c)). The other four minima along the $\pm x$ and $\pm y$ project onto the points between Γ and the zone boundary Z, i.e., to $k = \pm 1.7 \frac{\pi}{a} \cos(\frac{\pi}{4}) = \pm 1.7 \frac{\pi}{a} (\frac{\sqrt{2}}{2}) = \pm 0.85 \frac{\pi}{a_{wire}}$, considering $a_{wire} = \frac{a}{\sqrt{2}}$ for $\langle 110 \rangle$ SiNWs. These points have an effective mass value being between the longitudinal and transverse masses which comes out $m^* = 0.55 m_o$ [3].

In addition to the band folding, with reducing size, the quantum confinement introduces an energy shift on the folded subbands such that the subbands are pushed away from their bulk values, resulting with the increase of the band gap. The magnitude of the energy shift is different for each point of the subband, depending on the effective mass of that point.¹ The subband point associated with the larger effective mass will be least shifted with the confinement.

For $\langle 100 \rangle$ and $\langle 110 \rangle$ SiNWs, both the heavy and the light conduction band electron masses project onto Γ -point. The remaining minima are projected onto a point between Γ and the zone boundary Z giving rise to an effective mass of mixed heavy and light character. Therefore, the conduction-band edge at Γ -point has a larger confinement plane effective mass than the off- Γ minima. For NWs of sufficiently small size, as the band is upshifting with the confinement, the Γ -point energy falls back and the material undergoes an indirect-to-direct band gap transition.

To sum up, for the $\langle 100 \rangle$ NWs, four of the six minima project onto Γ -point and the rest two project onto points that are also close to Γ ($\pm 0.3 \Gamma Z$). For the $\langle 110 \rangle$ NWs, only two minima project onto Γ -point and the rest project to a far beyond point ($\pm 0.85 \Gamma Z$). Thus, there is a less effective folding and a weaker

¹To clarify, we might consider the particle-in-a-box model. The energy levels are given by $E = \frac{\hbar^2}{2m^*} (\frac{\pi^2 n^2}{L^2})$. If the well length L is decreased by increasing the confinement, the shift in the energy ΔE is larger, if m^* is smaller. In non-parabolic bands, m^* is wave vector dependent so that the shift ΔE depends on the dispersion point.

direct band gap character in the $\langle 110 \rangle$ Si NWs in comparison to $\langle 100 \rangle$ NWs.

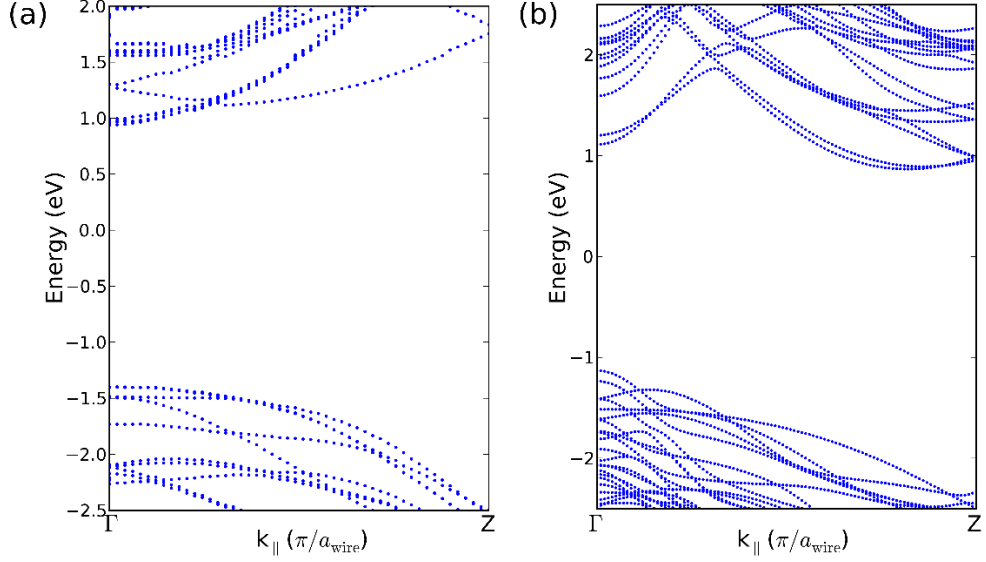


Figure 3.4: Dispersion curves of 2 nm diameter Si NWs along (a) $\langle 100 \rangle$ and (b) $\langle 110 \rangle$ directions. For $\langle 100 \rangle$ NW both band edges are located at Γ -point resulting with a direct band gap, whereas for $\langle 110 \rangle$ NW, the off- Γ minimum leads to an indirect gap. Note that the energy scales are different. As we discuss in Sec. 3.3, the band edges are aligned with respect to those of bulk Si.

Fig. 3.4 illustrates the electronic band structures near the band gap for the $\langle 100 \rangle$ and $\langle 110 \rangle$ Si NWs with 2 nm diameters. As expected, for $\langle 100 \rangle$ NW both the conduction band minimum (CBM) and valence band maximum (VBM) are settled down at Γ -point, giving rise to a direct band gap. As predicted by the zone folding discussion the second CBM is located around $0.3\Gamma Z$. Nevertheless, for $\langle 110 \rangle$ NW, we obtain an indirect gap. Notably, the CBM reveals at $\pm 0.85\Gamma Z$. That is the projection point for the four of the six minima as predicted by the band folding discussion. Our finding of the indirect band gap of embedded $\langle 110 \rangle$ Si NWs contradicts with the folding expectations as well as H-passivated results [3, 5, 54].

To clarify the discrepancy, we address a representative supercell filled with only Si atoms to elaborate on the band folding within LCBB framework. As seen in Fig. 3.5, in this case the band folding to the Γ -point reveals as expected with the proper effective mass of $m^* = 0.19 m_o$ (calculated by the curvature method)

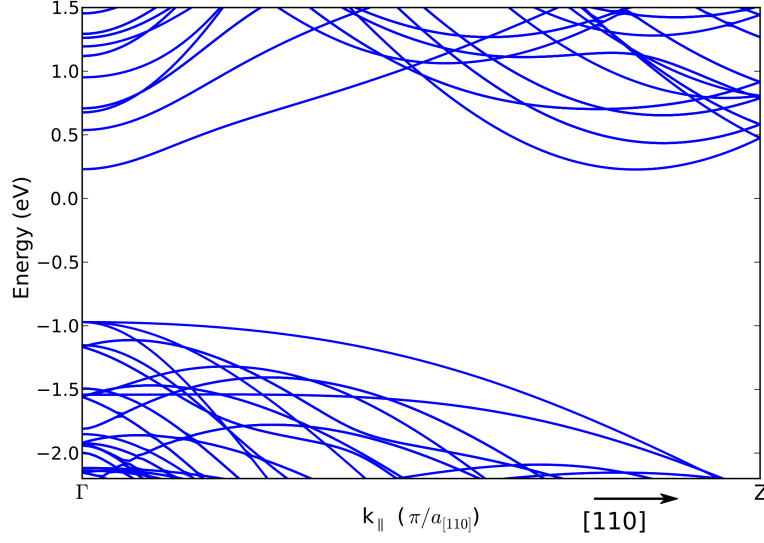


Figure 3.5: The folded band structure of bulk Si along the $\langle 110 \rangle$ direction. A representative supercell is filled with only Si atoms so that the band structure of bulk Si is folded.

and two-fold degeneracy. Therefore, our assertion is that the oxide passivation introduces an energy shifting different than both H-passivation case and effective mass theory-based prediction so that in the embedded $\langle 110 \rangle$ NWs the band ends up as indirect. This distinctive behavior in turn leads to the different anisotropic ordering of embedded Si NWs.

Here, we would like to comment on two points: (i) Considering the results of DFT calculations [5, 54], the energy difference between the direct and indirect band gaps of Si NWs are about 0.5 eV at 1 nm diameter, falls to about 0.25 eV at 2.5 nm and less than 0.1 eV beyond the 3 nm diameters. Thus, our calculations (referring Fig. 3.1) are still in accord with DFT calculations, concerning their second (indirect) CBM. (ii) In regard to H-passivated $\langle 110 \rangle$ Si NWs, although the CBM is located at Γ -point, the nature of the band gap is “quasi-direct” [2, 10]. Due to the very low density of states at Γ -point conduction band valley [2, 10] and vanishingly small dipole transition matrix elements of those direct transitions [4, 143], the actual nature of the band gap remains indirect. In our calculations, we correctly attain this indirect conduction band valley and can represent the actual device behavior characteristics of $\langle 110 \rangle$ Si NWs.

In Ref. [129] the electronic structure of oxide-sheathed Si NWs has been compared with reference H-passivated Si NWs. According to their results, for both $\langle 100 \rangle$ - and $\langle 111 \rangle$ -oriented Si NWs the band gaps shrink in comparison to the reference H-passivated ones, whereas for $\langle 112 \rangle$ -aligned Si NWs the band gap is almost identical, and for $\langle 110 \rangle$ -aligned Si NWs the band gap increases even. One difficulty we face in attempting to reproduce their oxide passivation results is that, although they give the diameters for the initial reference H-passivated Si NWs, the corroding of the cores under oxidation makes it hard to extract the mean diameters of the final oxidized structures. Given the fact that only one calculation was provided in that work for each orientation, more extensive first principles calculations are required to extract the effects of oxide passivation on the electronic structure of Si NWs.

3.2 Results on Si Nanowire Networks

Next, we investigate the crossings of Si NWs as building blocks of Si NWNs. The branched Si NWs synthesized so far [93, 94, 97] have larger diameters (> 20 nm) and prefers to grow in the $\langle 111 \rangle$ crystalline directions. Nevertheless, various *single* Si NW experiments [26, 28, 1, 29] indicates that at sub-10 nm diameters regime the occurrence of $\langle 110 \rangle$ -alignment surpass the other directions, while $\langle 111 \rangle$ and $\langle 112 \rangle$ alignments are more growth technique dependent. This behavior is also consistent with theoretical predictions [144]. Within this setting, for sub-10 nm size regime, our results are mainly referred for crossings of $\langle 110 \rangle$ -oriented NWs, even though we have performed calculations for crossings of $\langle 100 \rangle$ -, $\langle 110 \rangle$ -, $\langle 111 \rangle$ -, and $\langle 112 \rangle$ -aligned NWs as well. Thus, the following discussions and conclusions are valid for all directions unless stated otherwise.

As Figs. 3.6 (a) and (c) illustrate, crossings of two or three NWs are positioned in our computational supercells. Considering the 3D periodic boundary conditions of LCBB method, the crossings assemble 2D or 3D continuous NWNs [Figs. 3.6 (b) and (d)]. We would like to note that the branched or crossing NWs are different than the crossed NWs [31, 145]. The latter is built up by putting a

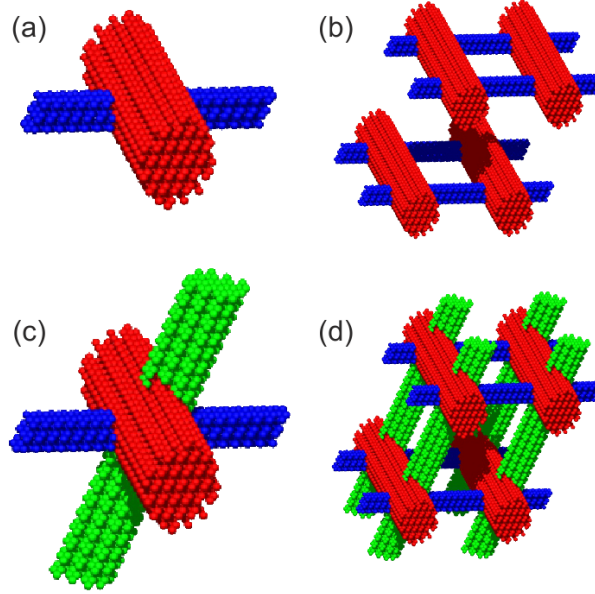


Figure 3.6: The computational supercells contain (a) two- or (c) three-wire crossings to build up (b) two- or (d) three-dimensional continuous Si NWNs, respectively. The wire orientations are in the family of $\langle 110 \rangle$ directions. (Reproduced with permission from Ref. [11]. Copyright 2013, AIP Publishing LLC.)

NW on top of another one without intersecting or “crossing” each other.

The crossings are again surrounded by an oxide matrix to passivate the Si dangling bonds. Unrelaxed structures are examined, i.e., the modifications of crossing morphologies by interface energy minimization are kept out of the scope of this work. Although, some reconstructions are possible for the realistic crossings, the electron microscopy images indicate that the intercrossings are still quite similar to ideal unrelaxed case [93, 97, 98]. Building ideal networks from the ideal NWs provides a test bed for probing the key factors determining the electronic structure of crossings and, finally, of NWNs. It should be noted that, in comparison to *single* NW calculations, the network supercells require large number of atoms. As an example, in the supercell of a crossing of three 1.03 nm thick NWs, the smallest crossing NW structure considered in this study, the supercell consists of 292 Si and 732 matrix atoms. These numbers grow to 3694 and 7970, respectively, in the case of the crossing of three 3 nm thick NWs.

Some representative results of our calculations are reported in Table 3.2. Here, Nos. 1, 4, and 7 correspond to single $\langle 110 \rangle$ Si NWs with diameters of 1.03 nm, 2.03 nm, and 2.94 nm, respectively. Nos. 2, 5, 8, and 9 are crossings of two NWs. The remaining structures are crossings of three NWs. Several conclusions can be drawn from this table. As seen from Nos. 1-3 and 4-6, the band gap values reduce with the increasing number of crossing wires. It means that with increasing branching, the carrier confinement diminishes due to the wave function extensions into the branches. Notably, from single NW to two-wire crossing, there is a significant reduction in the band gap whereas as an additional third NW is introduced to the crossing, the further reduction is minor (Nos. 1-3). As another feature, regarding structures Nos. 8 and 9, we observe that the band gap values are mostly dominated by the thicker NW of the crossing. In structure No. 9 the gap is determined almost completely by the thicker NW, though in structure No. 8, the thin NW induces still a marginal band gap reduction. The same behavior is valid for three-NW crossings (Nos. 10 and 12) that is, the band gap values are dominated by the thickest NW of the crossing while the others yet strive to reduce the gap.

To unambiguously clarify the effect of crossing, we include the test case that the NWs in the supercell do not touch each other (data shown in brackets in Table 3.2), and are even detached by at least 1 nm to prevent possible interactions. The non-crossing case results unequivocally reveal that the reduction of the band gaps is not due to the increase of the number of Si atoms in the supercell, but rather a consequence of the crossing. The non-crossing case computations indicate that (i) if the diameters are the same, the number of NWs in the supercell does not affect the calculated gap, (ii) if the NW diameters are distinct, the bandgap is exactly determined by the thickest NW.

3.2.1 A band gap estimator for Si NW Networks

Our calculations provide an exhaustive data set on the band gaps of NW-crossings which becomes rewarding, if it can be consolidated into a generalized form of Eq. (3.1) to estimate the band gap values of Si NWNs. As we remain on the

Table 3.2: Band gap energies for single Si NWs (No. 1, 4, 7) as well as for two-wire (No. 2, 5, 8, 9) and three-wire crossings (No. 3, 6, 10-14). Non-crossing bandgap value for each case is quoted in brackets.

No.	Wire diameters			E_g (eV)	
	d_1 (nm)	d_2 (nm)	d_3 (nm)		
1	1.50	-	-	2.40	-
2	1.50	1.50	-	2.18	[2.40]
3	1.50	1.50	1.50	2.11	[2.40]
4	2.03	-	-	1.99	-
5	2.03	2.03	-	1.84	[1.99]
6	2.03	2.03	2.03	1.73	[1.99]
7	2.94	-	-	1.57	-
8	1.50	2.03	-	1.96	[1.99]
9	1.50	2.94	-	1.57	[1.57]
10	1.50	1.50	2.03	1.85	[1.99]
11	1.50	2.03	2.03	1.81	[1.99]
12	1.50	1.50	2.94	1.57	[1.57]
13	1.50	2.03	2.94	1.56	[1.57]
14	2.03	2.03	2.94	1.55	[1.57]

reign of quantum size effect, the general dependence of band energies on structure dimensions should be similar to the case of single NWs. Following Eq. (3.1), we propose for the band gap E_g of N crossing NWs,

$$E_g = E_g^{\text{bulk}} + C \left(\sum_{i=1}^N d_i^\beta \right)^{-\alpha/\beta}, \quad (3.2)$$

where E_g^{bulk} is the band gap energy of bulk silicon and the d_i is the diameter of the NW indexed by i . The C and α are fitting parameters inherited from Eq. (3.1). Thus, only one additional parameter β has been introduced, within the impression of generalized mean (see App. A.3), which dictates the contributions of each NW, i.e., the larger the β value, the stronger the influence of the thickest NW on the band gap. Yet, the specific value of β hinges on the material-dependent atomic potentials and hence the case-specific manifestation of confinement effect.

For a single NW ($N = 1$), Eq. (3.2) simplifies to the conventional form of Eq. (3.1) which suggest that $\{C, \alpha\}$ of single NWs (as tabulated in Table 3.1)

can also be used for Eq. (3.2). Regarding the sensitivity to β , even in the strong confinement regime (~ 1 nm diameter), the band gap varies only by ± 0.1 eV when β varies in the range 4 to 7. With reference to our alignment analysis, we suggest to employ $\beta=5.5$ for $\langle 110 \rangle$, $\langle 111 \rangle$, and $\langle 112 \rangle$ crossings, however, for $\langle 100 \rangle$ crossings $\beta=4$ offers better performance. Fig. 3.7 shows the calculated data points and corresponding plots of Eq. (3.2) for 2D networks ($N = 2$), with $\beta=5.5$, whereas Fig. 3.8 shows the same for 3D networks ($N = 3$). The overall attainment of Eq. (3.2) is quite satisfying with the expected deviations for the very small sizes as we discussed in the single NW case.

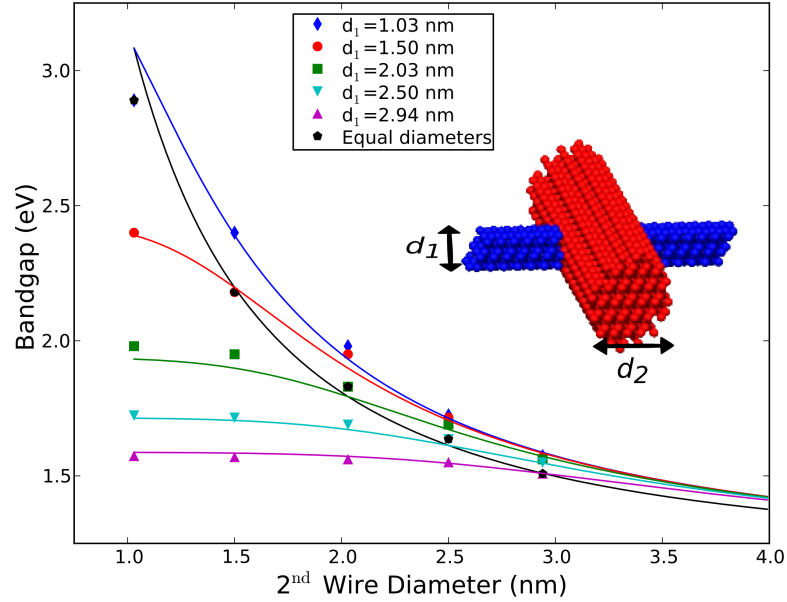


Figure 3.7: Band gap values for two-wire crossings. The calculated data points are shown with the markers, the lines are obtained via Eq.(3.2) ($\beta=5.5$ is used, see also Table 3.1). The crossing wire alignments are along $\langle 110 \rangle$ directions.

3.3 A note on the band lineups

An important aspect of material interfaces is the band lineups, i.e., the relative alignments of the band edges. The band lineup, or offset, dictates the effective barrier for the carrier transport across the interface [146]. In this regard, planar

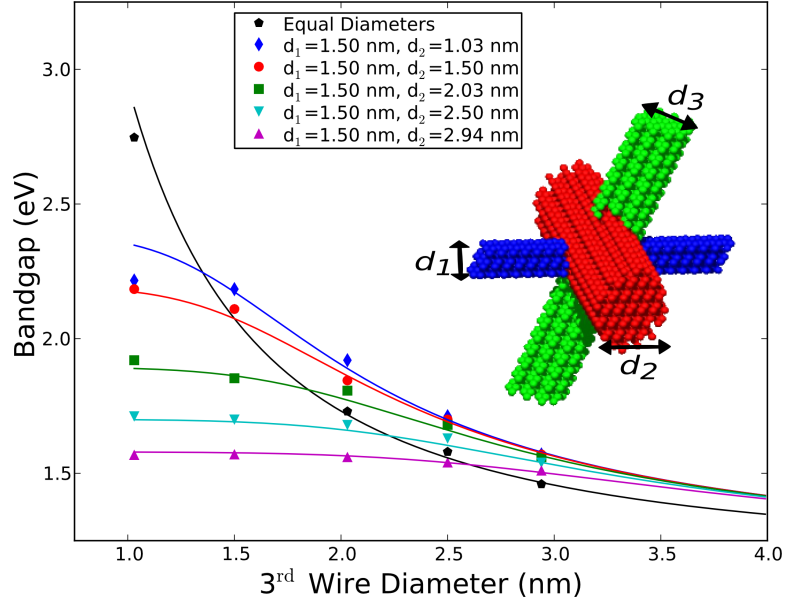


Figure 3.8: Same as Fig. 3.7 but for three-wire crossings. (Reproduced with permission from Ref. [11]. Copyright 2013, AIP Publishing LLC.)

Si/SiO₂ interface has been well-investigated [147, 148, 149, 150]. Nevertheless, the interfacial properties of nanostructures are rather different than the planar interface [151, 129], since the former compromises several different crystallographic orientations with curved interfaces. The work of Ref. [151] studies the interfacial electronic properties of Si NCs embedded in silica. The authors give the spatial variation of VB- and CB-edges along the radial direction through the interface. However, to the best of our knowledge there have not been such a study for the embedded Si NWs and NWNs.

As we briefly discuss in Sec. 3.1 in conjunction with the inset of Fig. 3.2, our computations inherently yield the band edge alignments of nanostructures in reference to those of bulk Si. As we point out therein the single Si NW band edge energies can be described by $E_{\text{VBE}} = C_{\text{VBE}} d^{-\alpha_{\text{VBE}}}$ and $E_{\text{CBE}} = E_g^{\text{bulk}} + C_{\text{CBE}} d^{-\alpha_{\text{CBE}}}$, where $\{C_{\text{VBE}}, \alpha_{\text{VBE}}\}$ and $\{C_{\text{CBE}}, \alpha_{\text{CBE}}\}$ are fitting parameters as listed in Table 3.1).

Considering device applications, as an alternative representation, we can obtain the band offsets of Si NWs with respect to bulk Si as $\Delta_{\text{VBO}}^{\text{Si}} = C_{\text{VBE}} d^{-\alpha_{\text{VBE}}}$ and $\Delta_{\text{CBO}}^{\text{Si}} = C_{\text{CBE}} d^{-\alpha_{\text{CBE}}}$. Moreover, since we set the bulk Si/SiO₂ VB (CB) offset as $E_{\text{VBO}} = 4.4$ eV ($E_{\text{CBO}} = 3.4$ eV), we can also provide the band offsets of Si NWs with respect to silica by simply writing $\Delta_{\text{VBO}}^{\text{SiO}_2} = -E_{\text{VBO}} - C_{\text{VBE}} d^{-\alpha_{\text{VBE}}}$ ($\Delta_{\text{CBO}}^{\text{SiO}_2} = E_{\text{CBO}} - C_{\text{CBE}} d^{-\alpha_{\text{CBE}}}$).

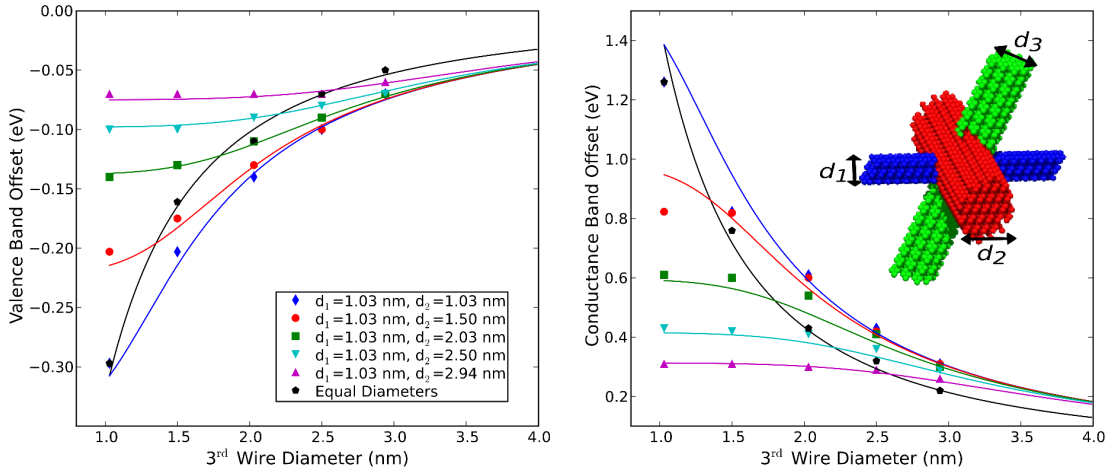


Figure 3.9: Valence and conduction band offsets for $\langle 110 \rangle$ three-wire crossings with respect to bulk Si band edges. The calculated values are shown with the markers whereas the estimation values based on the single nanowire parameters are plotted with the curves. Note that the energy scales are different.

Remarkably, the form of Eq. (3.2) can again be invoked such that the expressions $\Delta_{\text{VBO}}^{\text{Si}} = C_{\text{VBE}} \left(\sum_{i=1}^N d_i^\beta \right)^{-\alpha_{\text{VBE}}/\beta}$ and $\Delta_{\text{CBO}}^{\text{Si}} = C_{\text{CBE}} \left(\sum_{i=1}^N d_i^\beta \right)^{-\alpha_{\text{CBE}}/\beta}$ will estimate the VB- and CB-offsets of NWNs in reference to bulk Si. In Fig. 3.9, we show the calculated band-offset values as data points and plot the corresponding estimations, employing $\{C_{\text{VBE}}, \alpha_{\text{VBE}}\}$ and $\{C_{\text{CBE}}, \alpha_{\text{CBE}}\}$ parameters of single Si NWs (given in Table 3.1) together with the same β values of band gap estimation. The figure reflects that the overall achievement of band edge estimation is as successful as the band gap estimation. More importantly, we note that, same as the case of single NWs (see the inset of Fig. 3.2), the main contribution to the band gaps come from the shift of CBEs whereas the VBEs stay close to bulk Si value.

Here, we give a rudimentary account on the band lineup of Si NWs and NWNs. Further studies, particularly focusing on the radial profile of band edges at the interface region, will guide to define an interface thickness rather than a sharp band-offset. Accordingly, the understanding of the interfaces will clarify the wave function penetration into the passivation region so that the effective diameter of NWs, in the theoretical works, can be redefined more properly [10].

A.3 Appendix: Generalized Mean

The estimation function of NWN is constructed considering the generalized mean [152], also known as the power mean, to express our conclusion that thickest wire dominates the bandgap while the narrower wires still contributing marginally. The generalized β -mean of a set of values $(x_1, x_2, \dots, x_N)$ is defined by the expression

$$M_\beta(x_1, x_2, \dots, x_N) = \left[\frac{1}{N} \sum_{i=1}^N x_i^\beta \right]^{1/\beta}. \quad (3.3)$$

The special cases of generalized mean includes: minimum ($\beta \rightarrow -\infty$), harmonic mean ($\beta = -1$), geometric mean ($\beta \rightarrow 0$), arithmetic mean ($\beta = 1$), quadratic mean ($\beta = 2$), and maximum ($\beta \rightarrow +\infty$).

Chapter 4

Kubo-Greenwood Formula for the Electronic Conductivity

Once the system dimensions are comparable to the carrier wavelength, the classical billiard ball-like treatments of particles can no longer be valid and the quantum mechanical wave properties begin to dictate the transport. Regarding the nanostructures studied in this work, the system sizes along the confinement directions are on the order of a few nanometers, which is also the size of electron wavelength. Henceforth, the quantum effects start to play a prominent role leading to formation of subbands with characteristic one-dimensional (1D) density of states (DOS). In this regime the transport should be described within a quantum mechanical framework.

The objective of this chapter is to provide an introduction to the quantum ballistic transport in the framework of Kubo-Greenwood (KG) formula. In Sec. 4.1, we discuss some general aspects of 1D quantum transport, which proceeds with a heuristic derivation of Landauer formula. After this warm-up, we supply the full derivation of KG-formula in Sec. 4.2. The subsequent Sec. 4.3 is devoted to the application of KG-formula to 1D ballistic transport. The important issues concerning the numerical implementation of KG-formula are presented in Sec. 4.4. Finally, in Sec. 4.4.1 we spend a few words on the convergence performance of

LCBB-calculated subbands and band structure, being essential for the transport computations.

4.1 Ballistic Transport in One-dimensional Systems

Due to the periodicity of the supercells, the 1D nanostructure considered computationally has infinite extension along the axial direction. Then, Bloch's theorem asserts that the electronic states have plane wave components along this direction and implies that the carriers propagate infinitely without any scattering. This consideration brings us to the reign of quantum ballistic transport. In real materials the transport involves scatterings. To stay in the ballistic regime, the mean free path of carriers, which is the average distance that a carrier traverse in between two subsequent scatterings, should be larger than the corresponding length scale of the nanostructure [153]. In this work, we assume the transport is always ballistic.

To gain some insight into the 1D transport, we start with considering a 1D channel that is free of any irregularities or scattering mechanisms along its extension so that the carriers can traverse the channel ballistically. The channel is connected to two leads. The leads can be considered as two large reservoirs and the connections are adiabatically tapered and totally nonreflecting. A bias voltage V is applied across the leads in order to make a current flow from left to right. That is, assuming the system is at zero temperature, the left source reservoir is filled up to energy level μ_l and the right drain reservoir up to μ_r , satisfying that $\mu_l - \mu_r = eV$. The current carried by the carriers with energy in the range E to $E + \delta E$ is

$$\delta I_+ = g_s e v(E) g(E) \delta E, \quad (4.1)$$

where g_s is the spin degeneracy, e is the charge of the carrier, $v(E)$ is the velocity along the channel and $g(E)$ is the 1D DOS. We can derive the explicit form $g(E)$

by recalling the basic quantum mechanics of a two-dimensionally quantized systems. Assuming the motion is quantized on the transverse xy -plane by infinitely high potential walls and is free along the z -axis, by Bloch Theorem, for a channel of length L_z , we can write

$$\psi(x, y, z) = \psi(x, y, z + L_z) = \psi(x, y, z)e^{ik_z L_z}, \quad (4.2)$$

where k_z is the wave vector along the z -direction. The Bloch theorem requires the condition that

$$k_z L_z = 2\pi n_z \Rightarrow k_z = \frac{2\pi n_z}{L_z} \quad \text{where} \quad n_z = 0, \pm 1, \pm 2, \dots \quad (4.3)$$

The 1D DOS can be obtained from the number of states,

$$n = \frac{k_z}{(2\pi/L_z)} = \frac{L_z k_z}{2\pi} \Rightarrow \frac{dn}{dk_z} = \frac{L_z}{2\pi}. \quad (4.4)$$

Then the unidirectional DOS per unit length¹ is

$$g(E) = \frac{1}{L_z} \frac{dn}{dE} = \frac{1}{L_z} \frac{dn}{dk_z} \frac{dk_z}{dE} = \frac{1}{2\pi\hbar v(E)}. \quad (4.5)$$

Substituting the expression of 1D DOS in Eq. (4.1), we observe that the velocity $v(E)$ terms cancel out or one can equally say that in 1D the multiplication of $v(E)$ and $g(E)$ terms is constant and equals to $\hbar^{-1}$. This allows to write the current as

$$\delta I_+ = \frac{g_s e}{h} \delta E. \quad (4.6)$$

As the states with energy in between μ_l and μ_r contribute to conduction, the total current through the channel is

$$I_+ = \int_{\mu_r}^{\mu_l} \frac{g_s e}{h} dE = \frac{g_s e}{h} (\mu_l - \mu_r) = \frac{g_s e^2}{h} V, \quad (4.7)$$

so that the conductance, defined as the ratio of the current I to the voltage V , $G = I/V$ is equal to

$$G = \frac{g_s e^2}{h}. \quad (4.8)$$

¹Here, differently from usual 1D density of states calculations, we consider only $k_z > 0$ values, since we are calculating the transport through only one particular direction. Alternatively, 2 can be kept in the numerator of Eq. (4.4) to include the momenta through both directions and then the final conductance should be divided by 2.

For a spin polarized system, i.e. with the spin degeneracy, $g_s=2$, we obtain the quantized conductance unit, $G_o = 2e^2/h$ [$(12.9\text{ k}\Omega)^{-1}$]. By the opening of yet another channel, the conduction increases a further G_o . In the case of N perfectly transmitting channels, all will contribute equally to the conduction, so that the total conductance will be

$$G = \frac{2e^2}{h} N. \quad (4.9)$$

The equipartition of the conduction channels is a characteristic feature of 1D ballistic transport. We note that, in this semiclassical approach the quantum nature, i.e., the confinement along two directions, manifest itself via the peculiar DOS of 1D nanostructures. The steplike conductance follows owing to the cancellation of velocity and DOS terms.

If the conductor is not perfect due to the scatterings, then the one-channel expression of Eq. (4.8) multiplies with the transmission probability of conducting medium,

$$G = \frac{g_s e^2}{h} T, \quad (4.10)$$

which is the well-known Landauer formula [154, 155]. This formula can be rewritten for the multiple conducting channels case as

$$G = \frac{g_s e^2}{h} \sum_n^N T_n, \quad (4.11)$$

where N is the number of conducting channels and T_n is the transmission probability of each channel. The Landauer formula expresses the conductance in terms of the scattering properties of the conducting medium [156]. The formula later derived within the framework of the linear response theory, starting from the KG-formula [157, 158].

The Landauer formula contradicts with the common physical intuition, in the sense that for a perfect conductor ($T = 1$), one expects zero resistance or an infinite conductance. However, the formula asserts that the conductance stays finite with the multiples of the quantized value of G_o . Later, the finite resistance is explained as a contact resistance originating from the mode differences of reservoirs and conducting medium [159].

In the case of non-ballistic transport, i.e., transport is degraded by various scattering mechanisms, the conductance plateaus will be deformed from the ideal steps as Eq. (4.10) suggests [160]. In this work, we consider the ideal ballistic transport case.

We would like to present an alternative derivation of Eq. (4.8) by employing another definition of density of states. i.e. $g(E) = \frac{1}{L_z} \sum_{n_z} \delta(E - E_{n_z})$ which rewrites Eq. (4.1) as

$$\delta I_+ = g_s e v(E) \frac{1}{L_z} \sum_{n_z} \delta(E - E_{n_z}). \quad (4.12)$$

The sum over n_z can be converted to a integral over k_z using the expression $k_z = \frac{2\pi n_z}{L_z}$ [as derived in Eq. (4.3)],

$$\delta I_+ = g_s e \frac{L_z}{2\pi} \frac{1}{L_z} \int_0^\infty v(E) \delta(E - E_{k_z}) dk_z \delta E. \quad (4.13)$$

As we discussed in Note 1, we again consider only $k_z > 0$ values in the integration. While integrating Eq. (4.13), we should be careful about the subbands which give more than one root for the Dirac delta function. Fig. 4.1 illustrates two representative bands. For a specific energy value, say E_F , the blue subband has two roots, whereas the red subband has only one root. Then, by equipartition theorem, at this energy level the blue subband contributes $2G_0$ and red gives only G_0 . To represent this case properly in Eq. (4.13), we can exploit the multiple root property of Dirac delta function as

$$\int f(x) \delta(g(x)) dx = \sum_i \int f(x_i) \frac{\delta(x - x_i)}{|g'(x_i)|} dx, \quad (4.14)$$

such that

$$\delta I_+ = \frac{g_s e}{h} \sum_{k_{z,i}}^{N_E} \int_0^\infty v(E_{k_{z,i}}) \frac{\delta(k_z - k_{z,i})}{\left| \frac{dE_{k_z}}{dk_z} \right|_{k_{z,i}}} dk_z \delta E, \quad (4.15)$$

where $k_{z,i}$ are the roots of $E = E_{k_z} \big|_{k_z=k_{z,i}}$ and N_E is the number of those roots.

Using the definition of group velocity, [161]

$$v_g = \frac{1}{\hbar} \frac{dE_{k_z}}{dk_z}, \quad (4.16)$$

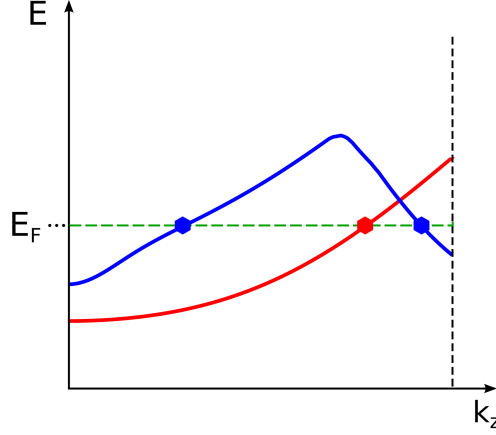


Figure 4.1: Schematic view of two representative subbands. The energy level E_F intersects the red subband only once, whereas there are two intersections for the blue one. Hence, at this energy level, the red will contribute G_0 to the conductance, that is $2G_0$ for the blue subband.

we again obtain the cancellation of terms which ends up with

$$\delta I_+ = \frac{g_s e}{h} N_E \delta E. \quad (4.17)$$

This relation explicitly indicates that when 1D subbands have multiple crossings with a given energy level then the conduction value takes the multiples of quantized unit $2e^2/h$. We obtain the conductance G as function of Fermi energy with KG-formula in the following section. Then the discussion about multiple roots becomes clearer. While $N_E=1$, we again obtain Eq. (4.8), then the aforementioned discussion continues to attain the derivation of the Landauer formula.

Despite its power, Landauer formula treats conducting medium as a scatter which requires the consideration of left and right leads [156]. That is difficult to implement within the LCBB method framework. Moreover, the Landauer formula is defined for a 1D conduction channel, whereas we would like to employ a more generic method that is valid also for the two- and three-dimensional systems. By this way, we can investigate the transport features of various embedded nanostructures such as nanocrystals, quantum wells as well as NW-based complex structures. Kubo-Greenwood formula obtained within the linear response regime is more convenient for us to bridge with our electronic structure computations.

4.2 Derivation of Kubo-Greenwood Formula

In this part we give the full derivation of Kubo-Greenwood (KG) formula [162, 163, 164]. As a matter of preference, this part can be skipped and one can safely continue from Eq. (4.37).

We want to calculate the static conductivity of a nanostructure via a fully quantum-mechanical formulation of transport theory. We assume the nanostructure is initially at equilibrium and then perturbed by an external voltage or by the corresponding electric field induced through the material. In the framework of linear response theory, the electric field $\mathbf{E}$ induces a current density $\mathbf{j}$ and those are related by the expression $\mathbf{j} = \sigma \mathbf{E}$ where the conductivity is defined by the proportionality constant σ which represents the response of the intrinsic properties of the medium to the effect of the external electric field. In general case the expression can be rewritten in the tensorial notation [156],

$$\mathbf{j} = \sigma \mathbf{E} \rightarrow j_\alpha = \sum_\beta \sigma_{\alpha\beta} E_\beta. \quad (4.18)$$

Accordingly, in order to calculate the conductivity σ of a medium, we should derive an expression in which $\mathbf{j}$ and $\mathbf{E}$ are proportional to each other in the first order. For that we can start with the expectation value of the current density which can be calculated by $\langle \mathbf{j} \rangle = Tr\{\rho \mathbf{j}\}$ using the statistical density operator, ρ of the medium [164]. To go into details of this trace operation, we consider a system which is initially at equilibrium and described by the equilibrium density operator ρ_o . The single-particle Hamiltonian of the system is

$$H_o = \frac{P^2}{2m_o} + V(\mathbf{r}), \quad (4.19)$$

where m_o is the free electron mass² and $V(\mathbf{r})$ contains the potentials due to the crystal structure, scatterings of the impurities, and electron-electron interactions within the mean field level. Introducing a basis of the single-particle eigenstates $|l\rangle$

²If the effective mass approximation (EMA) is applied in the initial equilibrium electronic structure calculations of the system, i.e., the Hamiltonian H_o is formulated with the effective mass of the carrier m^* and the single-particle basis vectors $|l\rangle$, the energy levels E_l , and occupation numbers f_l are obtained by means of EMA, then m_o should be m^* in this and the following expressions.

of the Hamiltonian H_o and since the density operator ρ_o has the same eigenstates as H_o , we can write

$$H_o|l\rangle = E_l|l\rangle, \quad \rho_o|l\rangle = f_l|l\rangle, \quad (4.20)$$

where f_l is the Fermi occupation number of the state $|l\rangle$.

In the presence of the external field, we add a perturbation term to the Hamiltonian of the system to represent the effect of the field

$$H = H_o + e\mathbf{E} \cdot \mathbf{r}. \quad (4.21)$$

However, for a macroscopic medium a more convenient way is to add the perturbation via the dynamical momentum operator $\boldsymbol{\pi}$, being proportional to the velocity operator $\mathbf{v}$. For a particle of charge of $-e$ in an electromagnetic field of the vector potential $\mathbf{A}$, the momentum operator is expressed as

$$\boldsymbol{\pi} = m_o\mathbf{v} = \mathbf{P} + e\mathbf{A}. \quad (4.22)$$

where we represented the electric field with the vector potential $\mathbf{A}$ which obeys $\mathbf{E} = -\dot{\mathbf{A}}$ and $\nabla \times \mathbf{A} = 0$, neglecting ant magnetic field, and considering a charge neutral system. Hence, for an electric field $\mathbf{E}$ of the time dependence $e^{-i\omega t}$, we can write $\mathbf{E} = i\omega\mathbf{A}$.

Then the Hamiltonian of the particle interacting with an electromagnetic field is given by

$$\begin{aligned} H &= \frac{\boldsymbol{\pi}^2}{2m_o} + V(\mathbf{r}) = \frac{(\mathbf{P} + e\mathbf{A})^2}{2m_o} + V(\mathbf{r}) \\ &= \frac{\mathbf{P}^2}{2m_o} + \frac{e}{2m_o} (\mathbf{P} \cdot \mathbf{A} + \mathbf{A} \cdot \mathbf{P}) + V(\mathbf{r}) + \mathcal{O}(A^2) \\ &= \frac{\mathbf{P}^2}{2m_o} + \frac{e}{m_o} \mathbf{A} \cdot \mathbf{P} + V(\mathbf{r}) + \mathcal{O}(A^2). \end{aligned} \quad (4.23)$$

Comparing with Eq. (4.19), we observe that the perturbation Hamiltonian is $H' = \frac{e}{m_o} \mathbf{A} \cdot \mathbf{P}$. Under the perturbation, the density operator alters to the form of $\rho = \rho_o + \delta\rho$ where $\delta\rho$ is a small deviation from the initial equilibrium ($\mathbf{A} = 0$) value due to the perturbation. We can assume that $\delta\rho$ has the same time dependence as the electric field.

Now after such a basic introduction of the initial equilibrium and perturbed states of the conducting medium, we can continue to the calculation of the expectation value of current density. For a spatially homogeneous system of volume V_{sc} , the current density is $\mathbf{j} = -e\mathbf{v}/V_{sc} = -e\boldsymbol{\pi}/m_oV_{sc} = -e(\mathbf{P} + e\mathbf{A})/m_oV_{sc}$. Then the expectation value of $\mathbf{j}$, using a basis $|l\rangle$ of eigenstates of H_o , is

$$\langle \mathbf{j} \rangle = tr\{\rho \mathbf{j}\} = \sum_{l'} \langle l' | (\rho_o + \delta\rho) \mathbf{j} | l' \rangle = \sum_{l, l'} [\langle l' | \rho_o | l \rangle \langle l | \mathbf{j} | l' \rangle + \langle l' | \delta\rho | l \rangle \langle l | \mathbf{j} | l' \rangle] . \quad (4.24)$$

In this relation the unknown term is the matrix element $\langle l | \delta\rho | l' \rangle$. In order to calculate that we can solve the quantum Liouville equation for the density operator [164]

$$i\hbar \frac{d\rho}{dt} = [H, \rho] + \left(\frac{\partial \rho}{\partial t} \right)_{rel} . \quad (4.25)$$

Here the term $\left(\frac{\partial \rho}{\partial t} \right)_{rel}$ reflects the relaxation processes of the excited system which can be described by adding phenomenological damping terms to the Liouville equation as $\left(\frac{\partial \rho}{\partial t} \right)_{rel} = -i\gamma(\rho - \rho_f)$ which means if the system is not far from the thermal equilibrium, ρ relaxes to its thermal equilibrium value ρ_f at a rate γ . This additional term leads to an exponential relaxation of ρ to ρ_f on the time scale $\hbar/\gamma$ [161]. Another way to interpret the relaxation rate γ is to consider the broadening of the energy levels of the excited system. Initially, the system has exact energy levels. However, when the system is perturbed (excited), the energy levels are not exact anymore, but will relax to exact states in time. In order to include the inexactness of the excited states, these states can be considered with an energy broadening of γ . Therefore, we rewrite Eq. (4.25) in the form

$$i\hbar \frac{d\rho}{dt} = [H, \rho] - i\gamma(\rho - \rho_f) . \quad (4.26)$$

In the matrix representation Eq. (4.26) is

$$\langle l' | i\hbar \frac{d\rho}{dt} | l \rangle = \langle l' | [H, \rho] | l \rangle - i\gamma \langle l' | \rho - \rho_f | l \rangle = \langle l' | [H_o + H', \rho_o + \delta\rho] | l \rangle - i\gamma \langle l' | \rho - \rho_f | l \rangle , \quad (4.27)$$

which leads to

$$\begin{aligned} \langle l' | i\hbar \frac{d\rho}{dt} | l \rangle &= \langle l' | H_o \rho_o + H_o \delta\rho + H' \rho_o + H' \delta\rho - \rho_o H_o - \rho_o H' - \delta\rho H_o - \delta\rho H' | l \rangle \\ &\quad - i\gamma \langle l' | \rho - \rho_f | l \rangle . \end{aligned} \quad (4.28)$$

Within the linear response theory, we neglect the terms of order $H'\delta\rho$ and employ the initial equilibrium eigenvalue equations [see Eq. (4.20)] to write

$$\begin{aligned}\langle l'|i\hbar\frac{d\rho}{dt}|l\rangle &= E_{l'}\langle l'|\delta\rho|l\rangle + f_l\langle l'|H'|l\rangle - f_{l'}\langle l'|H'|l\rangle - E_l\langle l'|\delta\rho|l\rangle \\ &\quad - i\gamma\langle l'|\rho - \rho_f|l\rangle \\ \langle l'|i\hbar\frac{d(\rho_o + \delta\rho)}{dt}|l\rangle &= (E_{l'} - E_l)\langle l'|\delta\rho|l\rangle - (f_{l'} - f_l)\langle l'|H'|l\rangle \\ &\quad - i\gamma\langle l'|\rho - \rho_f|l\rangle.\end{aligned}\tag{4.29}$$

For the left-hand side, we can employ that $\delta\rho$ has the same time dependence $e^{-i\omega t}$ as the electric field and $\frac{d}{dt}\rho_o = 0$, and for the right-hand side, $\rho - \rho_f = (\rho_o + \delta\rho) - (\rho_o + \delta\rho_f) = \delta\rho - \delta\rho_f$. Furthermore, for $\delta\rho_f$, again by solving the Liouville equation while keeping only the linear terms, we can show that,

$$\begin{aligned}\langle l'|i\hbar\frac{d\rho_f}{dt}|l\rangle &= \langle l'|[H, \rho_f]|l\rangle = \langle l'|[H, \rho_o + \delta\rho_f]|l\rangle = \langle l'|[H', \rho_o] + [H_o, \delta\rho_f]|l\rangle \\ \Rightarrow (f_l - f_{l'})\langle l'|H'|l\rangle + (E_{l'} - E_l)\langle l'|\delta\rho_f|l\rangle &= 0 \\ \Rightarrow \langle l'|\delta\rho_f|l\rangle &= \frac{(f_{l'} - f_l)}{(E_{l'} - E_l)}\langle l'|H'|l\rangle.\end{aligned}$$

With these arrangements, we can rewrite Eq. (4.29) in the form of

$$\begin{aligned}i\hbar(-i\omega)\langle l'|\delta\rho|l\rangle &= (E_{l'} - E_l)\langle l'|\delta\rho|l\rangle - (f_{l'} - f_l)\langle l'|H'|l\rangle - i\gamma\langle l'|\delta\rho|l\rangle \\ &\quad + i\gamma\frac{(f_{l'} - f_l)}{(E_{l'} - E_l)}\langle l'|H'|l\rangle,\end{aligned}\tag{4.30}$$

from which we can write the matrix element of $\delta\rho$ as

$$\langle l'|\delta\rho|l\rangle = \frac{(E_{l'} - E_l - i\gamma)}{(E_{l'} - E_l - \hbar\omega - i\gamma)}\frac{(f_{l'} - f_l)}{(E_{l'} - E_l)}\langle l'|H'|l\rangle.\tag{4.31}$$

The next task is to insert this matrix element into Eq. (4.24) to calculate the expectation value of the current density and eventually the conductivity. Rewriting Eq. (4.24), also using the definition $\mathbf{j} = -e(\mathbf{P} + e\mathbf{A})/m_oV_{sc}$ and $H' = \frac{e}{m_o}\mathbf{A} \cdot \mathbf{P}$, we have³

$$\begin{aligned}\langle \mathbf{j} \rangle &= \sum_{l,l'} \left[\langle l'|\rho_o|l\rangle \langle l|\frac{-e(\mathbf{P}+e\mathbf{A})}{m_oV_{sc}}|l'\rangle \right. \\ &\quad \left. + \frac{(E_{l'} - E_l - i\gamma)}{(E_{l'} - E_l - \hbar\omega - i\gamma)}\frac{(f_{l'} - f_l)}{(E_{l'} - E_l)}\langle l'|\frac{e}{m_o}\mathbf{A} \cdot \mathbf{P}|l\rangle \langle l|\frac{-e(\mathbf{P}+e\mathbf{A})}{m_oV_{sc}}|l'\rangle \right],\end{aligned}\tag{4.32}$$

³As we discussed in Note 2, when the EMA is applied m_o should be replaced with m^* . For a parabolic band m^* is constant and can be taken out of bra-kets, whereas for nonparabolic bands obviously the effective mass tensor m^* is not a constant value. Hence, it should be kept inside the bra-kets and treated similar to momentum operator.

with $\mathbf{E} = i\omega\mathbf{A}$ and keeping only the terms which are linearly proportional to the external field, we can write down the conductivity tensor

$$\begin{aligned}\sigma_{\alpha\beta} &= \frac{ie^2}{m_o V_{sc}\omega} \sum_{l,l'} \left[f_l \delta_{ll'} + \frac{1}{m_o} \frac{(E_{l'} - E_l - i\gamma)}{(E_{l'} - E_l - \hbar\omega - i\gamma)} \frac{(f_{l'} - f_l)}{(E_{l'} - E_l)} \langle l' | P_\alpha | l \rangle \langle l | P_\beta | l' \rangle \right] \\ &= \frac{ie^2}{m_o V_{sc}\omega} \left[\sum_l f_l + \frac{1}{m_o} \sum_{l,l'} \frac{(E_{l'} - E_l - i\gamma)}{(E_{l'} - E_l - \hbar\omega - i\gamma)} \frac{(f_{l'} - f_l)}{(E_{l'} - E_l)} \langle l' | P_\alpha | l \rangle \langle l | P_\beta | l' \rangle \right].\end{aligned}\quad (4.33)$$

In order to simplify this relation, we can use the Heisenberg equation of motion $i\hbar v_\alpha = \frac{i\hbar}{m_o} \pi_\alpha = \frac{i\hbar}{m_o} (P_\alpha + eA_\alpha) = [r_\alpha, H]$ where the subscript α denotes the directions. Here we note that $\frac{i\hbar}{m_o} (P_\alpha + eA_\alpha) = [r_\alpha, H] = [r_\alpha, H_o + \frac{e}{m_o} \mathbf{A} \cdot \mathbf{P}] = [r_\alpha, H_o] + \frac{e}{m_o} A_\alpha [r_\alpha, P_\alpha] = [r_\alpha, H_o] + \frac{i\hbar e}{m_o} A_\alpha$ so that we can simply use $\frac{i\hbar}{m_o} P_\alpha = [r_\alpha, H_o]$ or in the matrix representation

$$\frac{i\hbar}{m_o} \langle l' | P_\alpha | l \rangle = \langle l' | [r_\alpha, H] | l \rangle = \langle l' | r_\alpha H - H r_\alpha | l \rangle = (E_l - E_{l'}) \langle l' | r_\alpha | l \rangle,$$

which leads to

$$\langle l' | r_\alpha | l \rangle = \frac{-i\hbar \langle l' | P_\alpha | l \rangle}{m_o (E_{l'} - E_l)}.$$

Combining this result with the identity $[x_\alpha, P_\beta] = i\hbar \delta_{\alpha\beta}$, we observe that

$$\begin{aligned}\langle l | x_\alpha P_\beta - P_\beta x_\alpha | l \rangle &= \sum_{l'} (\langle l | x_\alpha | l' \rangle \langle l' | P_\beta | l \rangle - \langle l | P_\beta | l' \rangle \langle l' | x_\alpha | l \rangle) = i\hbar \delta_{\alpha\beta} \\ \sum_{l'} \left(\frac{-i\hbar}{m_o (E_l - E_{l'})} \langle l | P_\alpha | l' \rangle \langle l' | P_\beta | l \rangle - \langle l | P_\beta | l' \rangle \frac{-i\hbar}{m_o (E_{l'} - E_l)} \langle l' | P_\alpha | l \rangle \right) &= i\hbar \delta_{\alpha\beta},\end{aligned}$$

so that we drive a sum rule

$$\sum_{l'} \frac{\langle l | P_\alpha | l' \rangle \langle l' | P_\beta | l \rangle}{(E_l - E_{l'})} = -\frac{m_o}{2} \delta_{\alpha\beta}. \quad (4.34)$$

Now notice that in the expression of Eq. (4.33), we have the summation term

$$\mathcal{S} = \frac{1}{m_o} \sum_{l,l'} \frac{(E_{l'} - E_l - i\gamma)}{(E_{l'} - E_l - \hbar\omega - i\gamma)} \frac{(f_{l'} - f_l)}{(E_{l'} - E_l)} \langle l' | P_\alpha | l \rangle \langle l | P_\beta | l' \rangle, \quad (4.35)$$

in which we can simply use

$$\frac{E_{l'} - E_l - i\gamma}{E_{l'} - E_l - \hbar\omega - i\gamma} = 1 + \frac{\hbar\omega}{E_{l'} - E_l - \hbar\omega - i\gamma}, \quad (4.36)$$

to obtain

$$\begin{aligned}\mathcal{S} = \frac{1}{m_o} \sum_{l,l'} \frac{(f_{l'} - f_l)}{(E_{l'} - E_l)} \langle l' | P_\alpha | l \rangle \langle l | P_\beta | l' \rangle \\ + \frac{1}{m_o} \sum_{l,l'} \frac{\hbar\omega}{(E_{l'} - E_l - \hbar\omega - i\gamma)} \frac{(f_{l'} - f_l)}{(E_{l'} - E_l)} \langle l' | P_\alpha | l \rangle \langle l | P_\beta | l' \rangle.\end{aligned}$$

Here, the first term can be simplified by the sum rule derived in Eq. (4.34) such that

$$\begin{aligned}\frac{1}{m_o} \sum_{l,l'} \frac{(f_{l'} - f_l)}{(E_{l'} - E_l)} \langle l' | P_\alpha | l \rangle \langle l | P_\beta | l' \rangle \\ = \frac{1}{m_o} \sum_{l'} f_{l'} \sum_l \frac{\langle l' | P_\alpha | l \rangle \langle l | P_\beta | l' \rangle}{(E_{l'} - E_l)} - \frac{1}{m_o} \sum_l f_l \sum_{l'} \frac{\langle l' | P_\alpha | l \rangle \langle l | P_\beta | l' \rangle}{(E_{l'} - E_l)} \\ = \frac{1}{m_o} \sum_{l'} f_{l'} \left(-\frac{m_o}{2} \delta_{\alpha\beta} \right) - \frac{1}{m_o} \sum_l f_l \left(\frac{m_o}{2} \delta_{\alpha\beta} \right) = - \sum_l f_l \delta_{\alpha\beta},\end{aligned}$$

where in the last step we change the dummy variables. Using this result in Eq. (4.33) and restoring the spin degeneracy factor g_s , we obtained a general relation for the conductivity tensor

$$\begin{aligned}\sigma_{\alpha\beta} = g_s \frac{ie^2}{m_o V_{sc} \omega} \left[\sum_l f_l - \sum_l f_l \delta_{\alpha\beta} \right. \\ \left. + \frac{1}{m_o} \sum_{l,l'} \frac{\hbar\omega}{(E_{l'} - E_l - \hbar\omega - i\gamma)} \frac{(f_{l'} - f_l)}{(E_{l'} - E_l)} \langle l' | P_\alpha | l \rangle \langle l | P_\beta | l' \rangle \right]. \quad (4.37)\end{aligned}$$

In particular, the real part of conductivity (denoting $Re[\sigma_{\alpha\beta}] = \tilde{\sigma}_{\alpha\beta}$) can be extracted using the identity $Re[\lim_{\gamma \rightarrow 0^+} (i/(x - i\gamma))] = -\pi\delta(x)$, such that

$$\tilde{\sigma}_{\alpha\beta}(T, E_F, \omega) = -g_s \frac{\pi\hbar e^2}{m_o^2 V_{sc}} \left[\sum_{l,l'} \frac{(f_{l'} - f_l)}{(E_{l'} - E_l)} \langle l' | P_\alpha | l \rangle \langle l | P_\beta | l' \rangle \delta(E_{l'} - E_l - \hbar\omega) \right]. \quad (4.38)$$

This expression is called the Kubo-Greenwood formula for the electronic conductivity [162, 163]. Due to the dependence of Fermi-Dirac distributions on T and E_F , the conductivity $\tilde{\sigma}_{\alpha\beta}$ intrinsically has the same dependence. We emphasize this fact by writing $\tilde{\sigma}_{\alpha\beta} \rightarrow \tilde{\sigma}_{\alpha\beta}(T, E_F, \omega)$. As we see for the two states $(|l\rangle$ and

$|l'\rangle$) involved in the expression, one must be occupied and the other unoccupied, else wise the difference of the Fermi occupation numbers will lead to a vanishing contribution. In the dc-limit $\omega \rightarrow 0$ and observing that $\frac{(f_{l'} - f_l)}{(E_{l'} - E_l)} = \left(\frac{\partial f}{\partial E}\right)_{E_l}$, we can rewrite Eq. (4.38) as

$$\tilde{\sigma}_{\alpha\beta}(T, E_F) = -g_s \frac{\pi \hbar e^2}{m_o^2 V_{sc}} \sum_{l, l'} \left(\frac{\partial f}{\partial E} \right)_{E_l} \langle l' | P_\alpha | l \rangle \langle l | P_\beta | l' \rangle \delta(E_{l'} - E_l), \quad (4.39)$$

As expected physically and expressed mathematically by the factor $\left(\frac{\partial f}{\partial E}\right)$, only the states in the vicinity of the Fermi level E_F has contribution to the integral, i.e., to the conduction. Using a further Delta function identity $\delta(E_l - E_{l'}) = \int_{-\infty}^{\infty} dE \delta(E - E_l) \delta(E - E_{l'})$, the conductivity can be expressed in a more conventional form

$$\tilde{\sigma}_{\alpha\beta}(T, E_F) = g_s \frac{\pi \hbar e^2}{m_o^2 V_{sc}} \int \sum_{l, l'} \left(-\frac{\partial f}{\partial E} \right) \langle l' | P_\alpha | l \rangle \langle l | P_\beta | l' \rangle \delta(E - E_l) \delta(E - E_{l'}) dE. \quad (4.40)$$

Once the KG-formula written in this form, it becomes clear that in the dc-limit ($\omega \rightarrow 0$), there is no intra-band contribution to the conductivity. Hence, despite the summation over (l, l') , the contribution comes only from the terms obeying $\delta_{l, l'}$. Keeping this in mind, nevertheless, in order to treat the Dirac delta functions properly, in the following expressions, we keep (l, l') summation instead of dropping it only over l . Once the Dirac delta functions treated properly, we can impose the Kronecker delta $\delta_{l, l'}$.

At the zero-temperature limit the Fermi-Dirac distribution function is a step function at the Fermi energy so that its derivative gives the Dirac delta function $\left(-\frac{\partial f}{\partial E}\right) = \delta(E - E_F)$. Using this fact in Eq. (4.40), we obtain the zero-temperature dc-conductivity

$$\tilde{\sigma}_{\alpha\beta}(T = 0, E_F) = g_s \frac{\pi \hbar e^2}{m_o^2 V_{sc}} \int \sum_{l, l'} \delta(E - E_F) \langle l' | P_\alpha | l \rangle \langle l | P_\beta | l' \rangle \delta(E - E_l) \delta(E - E_{l'}) dE, \quad (4.41)$$

or integrating over energy E in order drop one of the Delta functions, we get

$$\tilde{\sigma}_{\alpha\beta}(T = 0, E_F) = g_s \frac{\pi \hbar e^2}{m_o^2 V_{sc}} \sum_{l, l'} \langle l' | P_\alpha | l \rangle \langle l | P_\beta | l' \rangle \delta(E_F - E_l) \delta(E_F - E_{l'}). \quad (4.42)$$

Here, reconsidering Eq. (4.40), we observe that with the employment of zero-temperature conductivity $\tilde{\sigma}_{\alpha\beta}(T=0, E_F)$, Eq. (4.40) can be rewritten as

$$\tilde{\sigma}_{\alpha\beta}(T, E_F) = \int \left(-\frac{\partial f}{\partial E} \right) \tilde{\sigma}_{\alpha\beta}(T=0, E) dE. \quad (4.43)$$

Hence, the finite-temperature conductivity is simply the energy average of the zero-temperature conductivity. The effect of increasing temperature on the conductivity will be just same as the thermal smearing of Fermi-Dirac distribution functions [165].

The KG-formula derived in both the finite-temperature and zero-temperature forms can be implemented numerically by broadening the Dirac delta functions either by Lorentzian or Gaussian broadening. The ingredients of both forms are the energy eigenvalues and corresponding momentum matrix elements, which are the outputs of electronic band structure calculations. Hence, we succeed to bridge the LCBB method with ballistic transport calculations. Within those forms KG-formula is quite general and can be applied to any dimensional systems.

4.3 KG-Formula for 1D Transport

We can employ the KG-formula for 1D transport to identify some computational implementation details. In the case of NWs, motion perpendicular to the NW direction is quantized so that the carriers are constrained to move through the NW. Setting the NW alignment along the z -axis, we need to calculate $\tilde{\sigma}_{zz}$. From the electronic structure calculations we know that for NWs there are two principal quantum numbers $(n_{\perp}, n_{\parallel})$ where $n_{\perp}$ represents the subband energy levels due to the transverse confinement and $n_{\parallel}$ gives the longitudinal dispersion through the 1D Brillouin zone (BZ) of NW (instead of specifying $n_{\perp}$ as n_{xy} and $n_{\parallel}$ as n_z , we keep them in general form). In Eq. (4.40), we can insert these quantum labels to obtain

$$\begin{aligned} \tilde{\sigma}_{zz}(T, E_F) = g_s \frac{\pi \hbar e^2}{m_o^2 V_{sc}} \int \sum_{n_{\perp}, n'_{\perp}, n_{\parallel}, n'_{\parallel}} \left(-\frac{\partial f}{\partial E} \right) \langle n'_{\perp} n'_{\parallel} | P_z | n_{\perp} n_{\parallel} \rangle \langle n_{\perp} n_{\parallel} | P_z | n'_{\perp} n'_{\parallel} \rangle \\ \times \delta(E - E_{n_{\perp} n_{\parallel}}) \delta(E - E_{n'_{\perp} n'_{\parallel}}) dE. \end{aligned} \quad (4.44)$$

Alternatively, to follow the general convention, $n_{\parallel}$ can be replaced by the wave vector $k_{\parallel}$ employing the relation $n_{\parallel} = \frac{L_z}{2\pi}k_{\parallel}$ where L_z is the length of the NW [as seen from Eq. (4.3)]. Also using n instead of $n_{\perp}$ for short hand notation, Eq. (4.44) alters to the form

$$\tilde{\sigma}_{zz}(T, E_F) = g_s \frac{\pi \hbar e^2}{m_o^2 V_{sc}} \int \left(\frac{L_z}{2\pi} \right)^2 \sum_{n, n', k_{\parallel}, k'_{\parallel}} \left(-\frac{\partial f}{\partial E} \right) \langle n' k'_{\parallel} | P_z | n k_{\parallel} \rangle \langle n k_{\parallel} | P_z | n' k'_{\parallel} \rangle \times \delta(E - E_{n k_{\parallel}}) \delta(E - E_{n' k'_{\parallel}}) dE. \quad (4.45)$$

Considering the dispersion of NWs, $k_{\parallel}$ is a continuous quantity, but for a chosen finite supercell it becomes discrete. This form can be easily combined with LCBB method, since we already have the energy dispersion $E_{n k_{\parallel}}$ and corresponding momentum matrix elements. Yet, we can reduce the computational load by analytically examining this equation. By this way, we can also gain insight into the physical meaning of the equation.

To keep the formulation general, we consider the case that each subband may intersect the Fermi level more than once. This is the behavior that we observe for the band structure of NWs (see for example Fig. 4.2). Thus, we again need to exploit the Dirac delta function property as given in Eq. (4.14). Inserting it in Eq. (4.45), we obtain

$$\tilde{\sigma}_{zz} = g_s \frac{\pi \hbar e^2}{m_o^2 V_{sc}} \int \left(\frac{L_z}{2\pi} \right)^2 \int \int \sum_{\substack{n, n' \\ k_{\parallel, n_i}, \\ k'_{\parallel, n'_i}}} \left(-\frac{\partial f}{\partial E} \right) \langle n' k'_{\parallel, n'_i} | P_z | n k_{\parallel, n_i} \rangle \langle n k_{\parallel, n_i} | P_z | n' k'_{\parallel, n'_i} \rangle \times \frac{2 \delta(k_{\parallel} - k_{\parallel, n_i})}{\left| \frac{dE_{n k_{\parallel}}}{dk_{\parallel}} \right|_{k_{\parallel}=k_{\parallel, n_i}}} \frac{2 \delta(k'_{\parallel} - k'_{\parallel, n'_i})}{\left| \frac{dE_{n' k'_{\parallel}}}{dk'_{\parallel}} \right|_{k'_{\parallel}=k'_{\parallel, n'_i}}} dk_{\parallel} dk'_{\parallel} dE, \quad (4.46)$$

where $k_{\parallel, n_i}$ and $k'_{\parallel, n'_i}$ are the roots of $E = E_{n k_{\parallel}}|_{k_{\parallel}=k_{\parallel, n_i}}$ and $E = E_{n' k'_{\parallel}}|_{k'_{\parallel}=k'_{\parallel, n'_i}}$, respectively. Notice that each root is doubly degenerate due to $\pm k_{\parallel}$ values. To reflect that we insert explicit 2 values before the Dirac delta functions, so in the rest we consider only $k_{\parallel, n_i} > 0$ roots that fall in a half Brillouin zone from center Γ to zone boundary Z . Here we also employed the fact that $k_{\parallel}$ is a continuous quantity and so that the sum $\sum_{k_{\parallel}}$ interchanges with the integral $\int dk_{\parallel}$. Performing

$k_{\parallel}$ and $k'_{\parallel}$ integrations

$$\tilde{\sigma}_{zz} = g_s \frac{\pi \hbar e^2}{m_o^2 V_{sc}} \int \left(\frac{L_z}{\pi} \right)^2 \sum_{\substack{n, n' \\ k_{\parallel}, n_i, \\ k'_{\parallel}, n'_i}} \left(-\frac{\partial f}{\partial E} \right) \frac{\langle n' k'_{\parallel}, n'_i | P_z | n k_{\parallel}, n_i \rangle \langle n k_{\parallel}, n_i | P_z | n' k'_{\parallel}, n'_i \rangle}{\left| \frac{dE_{nk_{\parallel}}}{dk_{\parallel}} \right|_{k_{\parallel}, n_i} \left| \frac{dE_{n'k'_{\parallel}}}{dk'_{\parallel}} \right|_{k'_{\parallel}, n'_i}} dE. \quad (4.47)$$

As the Dirac delta functions treated safely, we can remember our comment on dc-limit [given following the Eq. (4.40)] that is the sum over (l, l') can be converted to sum over only l by imposing $\delta_{l, l'}$, i.e., $\delta_{n, n'} \delta_{k_{\parallel}, k'_{\parallel}}$ in this case. That is indeed supported in 1D transport with the fact that for 1D nanostructures the momentum matrix elements have the property that $\langle n' k'_{\parallel} | P_{\alpha} | n k_{\parallel} \rangle = \langle n' k'_{\parallel} | P_{\alpha} | n k_{\parallel} \rangle \delta_{k'_{\parallel}, k_{\parallel}}$ thanks to the plane wave normalizations (also shown in App. A.2 with in the context of LCBB method). Accordingly, imposing $\delta_{n, n'} \delta_{k_{\parallel}, k'_{\parallel}}$, we rewrite Eq. (4.47) as

$$\tilde{\sigma}_{zz}(T, E_F) = g_s \frac{\pi \hbar e^2}{m_o^2 V_{sc}} \int \left(\frac{L_z}{\pi} \right)^2 \sum_{n, k_{\parallel}, n_i} \left(-\frac{\partial f}{\partial E} \right) \frac{|\langle n k_{\parallel}, n_i | P_z | n k_{\parallel}, n_i \rangle|^2}{\left| \frac{dE_{nk_{\parallel}}}{dk_{\parallel}} \right|_{k_{\parallel}, n_i}^2} dE. \quad (4.48)$$

As we eliminated two Dirac delta functions, this form is more convenient numerically as opposed to Eq. (4.45).

In an experiment one measures the resistance R or conductance G , rather than the conductivity σ . For a NW of length L_z and cross-sectional area of A , the conductivity and conductance are related by $G = \frac{\sigma A}{L_z}$. Employing this relation, we can switch to the conductance G ,

$$G_{zz}(T, E_F) = g_s \frac{\hbar e^2}{2\pi m_o^2} \int \sum_{n, k_{\parallel}, n_i} \left(-\frac{\partial f}{\partial E} \right) \frac{|\langle n k_{\parallel}, n_i | P_z | n k_{\parallel}, n_i \rangle|^2}{\left| \frac{dE_{nk_{\parallel}}}{dk_{\parallel}} \right|_{k_{\parallel}, n_i}^2} dE. \quad (4.49)$$

At the final step, we also divide the total result by 2, remembering that though in the derivation, we include both $+k_{\parallel}$ and $-k_{\parallel}$ values, we are interested only with the transport to one specific direction. We employ this simplified form of KG-formula in our quantum ballistic transport computations.

For the finite-temperature calculations, we exploit the energy derivative of

Fermi-Dirac distribution,

$$-\frac{\partial f}{\partial E} = \frac{1}{k_B T} \frac{e^{(E-E_F)/k_B T}}{[e^{(E-E_F)/k_B T} + 1]^2} = \frac{1}{4k_B T} \operatorname{sech}^2 \left[\frac{E - E_F}{2k_B T} \right]. \quad (4.50)$$

For the zero-temperature case, inserting $\delta(E - E_F)$ and performing the energy integration, we obtain

$$G_{zz}(T=0, E_F) = g_s \frac{\hbar e^2}{2\pi m_o^2} \sum_{n, k_{\parallel, i}} \frac{|\langle n k_{\parallel, n_i} | P_z | n k_{\parallel, n_i} \rangle|^2}{\left| \frac{dE_{nk_{\parallel}}}{dk_{\parallel}} \right|_{k_{\parallel, n_i}}^2}, \quad (4.51)$$

keeping in mind that then the roots should be calculated at Fermi energy, i.e., $E_F = E_{nk_{\parallel}}|_{k_{\parallel, n_i}}$.

As a final remark we would like to show that one can gently go from the last form of KG-formula to Eq.(4.9). For the simplicity, we assume the subbands are parabolic, so the Fermi energy crosses each subband only once, i.e., at a specific $k_{\parallel, n^*}$ for each subband n . This drops the $k_{\parallel, i}$ sum. By observing that $\langle n k_{\parallel, n^*} | P_z | n k_{\parallel, n^*} \rangle / m_o = v_{g, n} |_{k_{\parallel, n^*}}$ and recalling the definition of group velocity [Eq. (4.16)], we can rewrite Eq. (4.51) as

$$G_{zz}(E_F) = g_s \frac{\hbar e^2}{2\pi} \sum_n \frac{\left[v_{g, n} |_{k_{\parallel, n^*}} \right]^2}{\left[\hbar v_{g, n} |_{k_{\parallel, n^*}} \right]^2}. \quad (4.52)$$

and inserting the spin degeneracy as $g_s = 2$, we re-obtain Eq. (4.9),

$$G_{zz}(E_F) = \frac{2e^2}{h} N, \quad (4.53)$$

where N is the number of crossed bands at a specific Fermi energy E_F . We notice that the velocity terms of denominator originate step by step from the Dirac delta functions of Eq. (4.44) which are representing DOS in essence. Hence, again the cancellation between the momentum and DOS brings us to Eq. (4.53).

4.4 Computational Considerations

When we are implementing Eq. (4.49), we need to set a parameter γ_F which seeks the roots $k_{\parallel, i}$ of expression $E_F = E_{nk_{\parallel}}|_{k_{\parallel, i}}$ by the condition that $|E_F - E_{nk_{\parallel, i}}| \leq \gamma_F$.

On the other hand, our preliminary investigation indicated that in order to obtain sharp conductance steps, ΔE_F values should be about a few meV, otherwise the steps smear out. This becomes essential especially when we investigate the temperature dependence of conductance. In order to indicate the sole effect of temperature, the computation should be clean of numerical smearings.

The interplay of ΔE_F and γ_F requires special attention such that: (i) as E_F scans through the energy range of a subband, the dispersion of the band should be so dense that for each E_F the relation $|E_F - E_{nk_{\parallel,i}}| \leq \gamma_F$ can catch an $E_{nk_{\parallel,i}}$, (ii) once an $E_{nk_{\parallel,i}}$ is found, then there would not be any more “solutions” from this γ_F neighborhood of $E_{nk_{\parallel,i}}$. Otherwise, there will be unphysical erroneous contributions to the conductance. The latter can be easily solved, but the former requires a dense-grid energy dispersion for the 1D BZ. For that, as we discuss in Ch. 2, we need to solve the separated Schrödinger equation on more $k_{\parallel}$ points so that $\Delta k_{\parallel}$ will be smaller. Instead, to keep the computational load lower, once the dispersion is converged the further increase of the number of $k_{\parallel}$ points can be achieved via the interpolation of energy dispersion data.

For the proper interpolation, however, first we need to label the subbands properly starting from Γ all through the BZ, and also the momentum matrix elements regarding the KG-formula. This is required since the eigenvalue solver gives the eigenenergies, at definite $k_{\parallel}$ points, only sorting with respect to their values without caring for their subband labels. The subband labeling can be done within the LCBB framework considering the overlap integrals of neighboring energy states. Considering the LCBB expansion of Eq. (2.19), we can calculate the cell-periodic overlap integral of two states, namely, $|nk_{\parallel}\rangle$ and $|n'k'_{\parallel}\rangle$ as

$$\mathcal{O}\{nk_{\parallel}, n'k'_{\parallel}\} = \sum_{\substack{l, l', \vec{k}_{\perp}, \\ \sigma, \vec{G}}} C_{l, \vec{k}_{\perp}, \vec{k}_{\parallel}, n}^{\sigma*} B_{l\vec{k}_{\perp}}^{\sigma}(\vec{G})^* C_{l, \vec{k}_{\perp}, \vec{k}'_{\parallel}, n'}^{\sigma} B_{l\vec{k}_{\perp}}^{\sigma}(\vec{G})$$

Starting from Γ -point, we scan the BZ. If the overlap integral of any two states with subband indices n and n' satisfies the condition that $|\mathcal{O}\{nk_{\parallel}, n'(k_{\parallel} + 1)\}| > 0.9$, then we label them with the same subband index. First panel of Fig. 4.2 shows the outcome of this identification for the challenging, multiply-crossing subbands of the $\langle 110 \rangle$ -aligned Si NW of diameter of 2 nm. Corresponding DOS

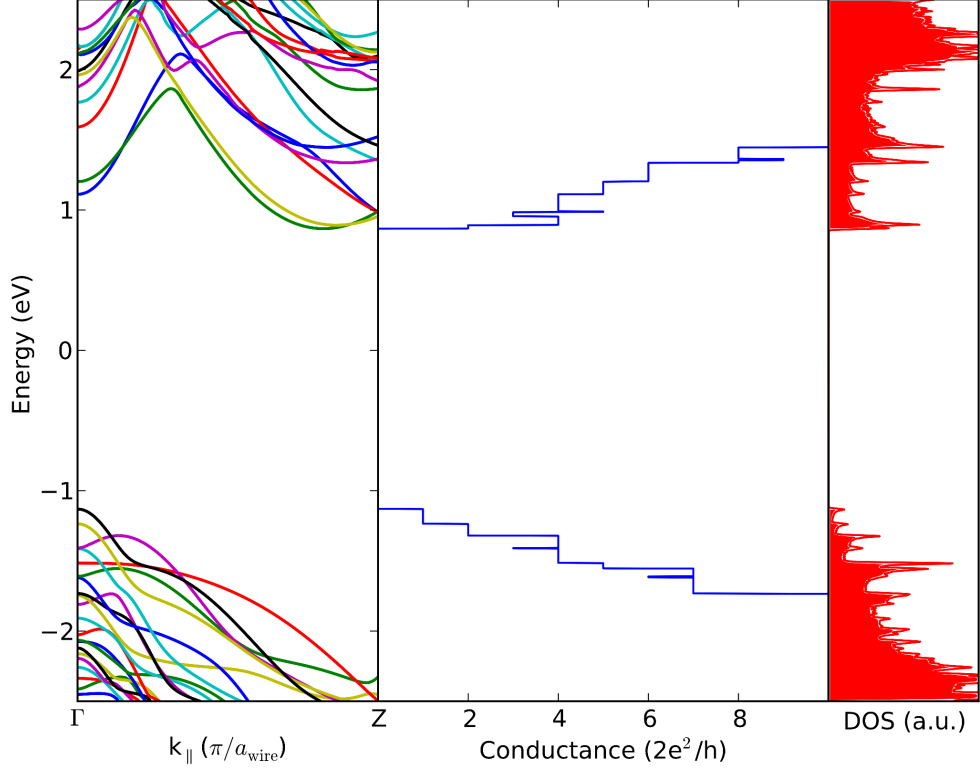


Figure 4.2: The calculated band structure, electronic conductance, and DOS of a $\langle 110 \rangle$ -aligned Si NW of diameter of 2 nm.

with broadening of 5 meV is given in the right panel in which the characteristic van Hove singularities of 1D DOS can be identified. In the middle panel, the zero-temperature conductance is presented. The conductance is computed via Eq. (4.51). The vertical energy axis of the middle panel displays the Fermi energy level. In the conduction band, for instance, with increasing Fermi energy more subbands open to transport so that the conductance increases. As seen from the conduction band edge, even very narrow conductance plateaus can be identified, once the ΔE_F and $\Delta k_{\parallel}$ are reduced accordingly. In this computation, both ΔE_F and γ_F are taken as 1 meV, $\Delta k_{\parallel}$ is set to $5 \times 10^{-4}(\pi/a_{\text{wire}})$.

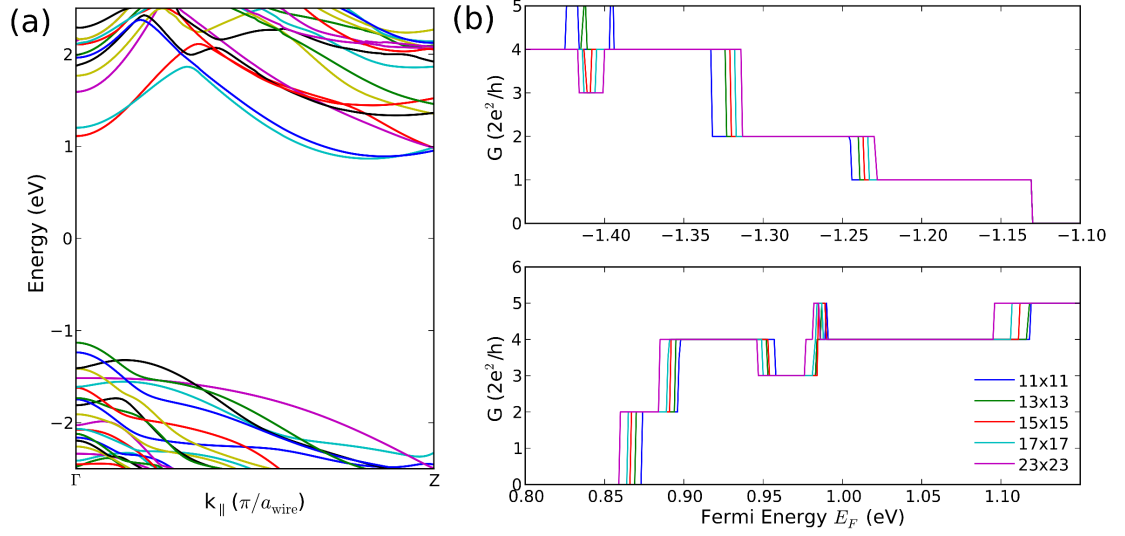


Figure 4.3: Calculated conductance values reflect the convergence of band dispersion. (a) Band structure of $\langle 110 \rangle$ -aligned Si NW of diameter of 2 nm, setting the number of $\vec{k}_\perp$ -points as 13×13 and $k_\parallel$ -points as 100. (b) the convergence of conductance with respect to number of in-plane $\vec{k}_\perp$ -points.

4.4.1 Convergence Performance of Energy Band Structure

The main ingredient of KG-formula is the energy dispersion $E_{nk_\parallel} = E_n(k_\parallel)$. Thus, its convergence is essential for the proper conductance calculations. Once its convergence is assured, then we can perform the interpolation mentioned above. As we discuss extensively in Sec. 2.3, the convergence has two aspects: the number of in-plane $\vec{k}_\perp$ -points and the number of $k_\parallel$ points to sample the 1D BZ of the NW. We give the detailed discussion of band edges in Sec. 2.3, here we seek how the band dispersion or subband edges converge within a narrow energy range just around the band gap. The conductance calculations provide an appropriate testbed for the convergence performance of subbands.

Both in Fig. 4.3 (a) and Fig. 4.4 (a) the band structure of $\langle 110 \rangle$ -aligned Si NW of diameter of 2 nm is given as a reference to (b) parts, setting number of $\vec{k}_\perp$ -points as 13×13 and $k_\parallel$ -points as 100. Fig. 4.3 (b) presents the convergence of

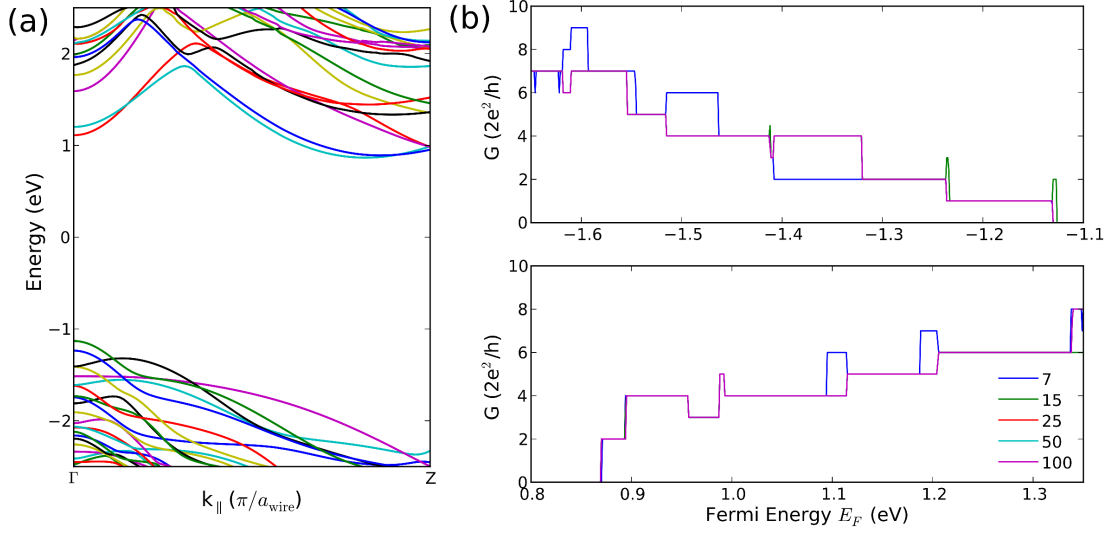


Figure 4.4: Same as Fig.4.3 but now (b) presents the convergence with respect to number of $k_{\parallel}$ -points, setting number of $\vec{k}_{\perp}$ -points as 13×13 .

conductance with respect to number of in-plane $\vec{k}_{\perp}$ -points. The valence band edge settles immediately and stays there, whereas edges of subbands progressively converges. Both the conduction band edge and subbands behave similar to valence subbands and slightly shift through lower energies as the number of sampling points increases. Yet, the shifts are around 10 meV when the number of sampling points are beyond 13×13 .

Fig. 4.3 (b) gives the convergence performance with respect to number of $k_{\parallel}$ -points. No change is observed once the number of $k_{\parallel}$ -points is beyond 25 which corresponds to $\Delta k_{\parallel} = 0.04(\pi/a_{\text{wire}})$. Yet, in the calculations of this thesis, we mostly set $\Delta k_{\parallel} = 0.01(\pi/a_{\text{wire}})$.

So far, we discuss the convergence performance from the energetics point of view. But besides, regarding the general form of KG-formula [see Eqs. (4.40) or (4.44)], the convergence and performance of momentum matrix elements are also of the same importance. Indeed, as we follow from Eqs. (4.50)-(4.53) in the case of 1D transport, the cancellation of velocity and DOS terms leads to trivial computations which only depends on the band structure. This introduces a tool for the convergence of wave functions. That is, we can compare the conductance

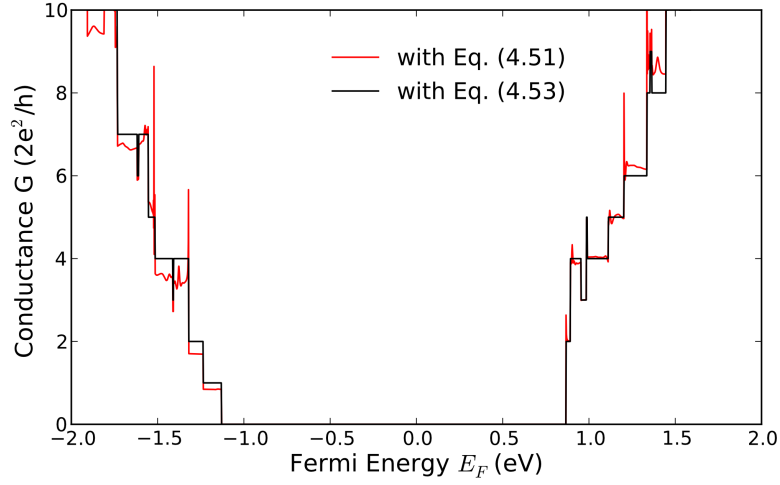


Figure 4.5: The conductance of $\langle 110 \rangle$ -aligned Si NW of diameter of 2 nm. Eq. (4.53) gives the ideal conduction steps. However, when the momentum matrix elements are calculated within the LCBB method by Eq. (A.11) and employed in Eq. (4.51), the ideal steps and plateaus are deformed.

results with the momentum matrix elements either calculated within the LCBB method (shown in App. A) or via the group velocity by $\langle nk_{\parallel} | P_z | nk_{\parallel} \rangle = m_o v_{g,n} | k_{\parallel} \rangle$. Fig. 4.5 shows the results of those computations for a $\langle 110 \rangle$ -aligned Si NW of diameter of 2 nm. As seen from the figure, though in general the calculated conductances are similar, there is an intriguing discrepancy, mostly in the hole conduction.

The discrepancy can be traced in Fig. 4.6 where we present the band structure and corresponding conductance and velocity values for the first conduction and valence subbands originating from Γ -point. As seen from the last column of velocity values the slight deviation of the momentum-derived velocity term with respect to derivative-derived one damages the characteristic cancellation of 1D transport and ends up with deformed conduction steps and plateaus.

Although, we have tried increasingly denser k -gridings, we have not succeeded to alleviate this deviation. This case reminds us once more the fundamental credo of numerical computations that *if there is any analytical simplification in the formulation that we can exploit, we should just do it before coding the numerics*.

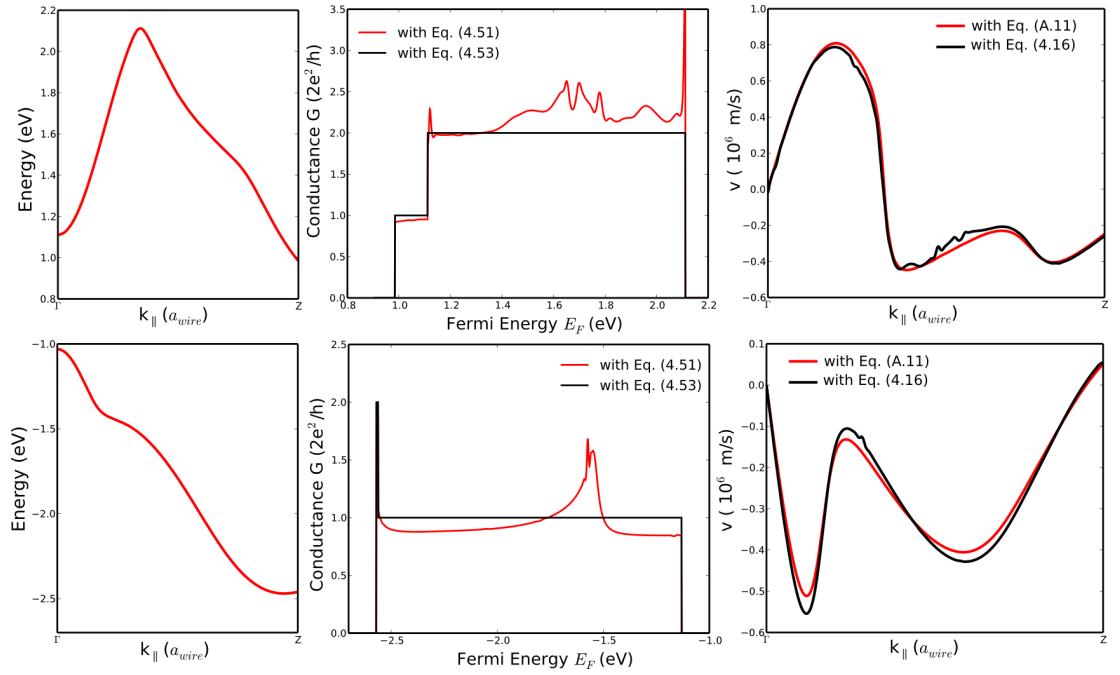


Figure 4.6: Band structure, conductance and velocity values for the first conduction and valence subbands originating from Γ -point. LCBB-calculated velocity values [via Eq. (A.11)] deviate from the derivative-derived velocities [via Eq. (4.16)]. The latter, basing on the band structure, indicates the proper values for which the characteristic cancellation of 1D transport satisfies and then ideal conduction steps are displayed.

Chapter 5

Carrier Localization and Transport Properties of NW-based Complex Nanostructures

Our results and analysis given in Ch. 3, for the Si NWs and NW networks (NWNs), are based on energetics. In this chapter, we seek to provide a deeper insight and understanding into those electronic structure data by examining the carrier localization and ballistic transport properties of some low-lying band edge states.

In Sec. 5.1, we consider single Si NWs and present results regarding the NW diameter dependence of ballistic conductance and effective mass as well as the temperature-related smearing of conductance within the ballistic regime. This is followed in Sec. 5.2 with the detailed investigation of Si NWNs. The band gap results of Ch. 3 are revisited and analyzed in the light of isosurfaces of carrier densities and ballistic transport calculations. In Sec. 5.3, our findings about the

NWNs are used to interpret the band edge characteristics of branched nanocrystals and NWs. Finally, in Sec. 5.4, we consider the carrier localization and transport dynamics of kinked NWs, a structure that has recently attached attention in some important experiments [166, 167, 168].

5.1 Tool benchmarking: single Si Nanowires revisited

As a starting point to our analysis of electronic transport properties, we compute the zero-temperature ballistic conductance of several diameter NWs as well as the electron (hole) effective mass at the CB (VB) edges along their axis. We calculate the conductances by employing Eq. (4.51). The effective masses are evaluated by the curvature method considering the definition $1/m^* = [1/\hbar^2][d^2 E_n(k_{\parallel})/dk_{\parallel}^2]$ where $E_n(k_{\parallel})$ is the energy dispersion relation and $k_{\parallel}$ is the wave vector along the dispersion direction [161]. We use a finite difference scheme, setting $\Delta k_{\parallel} = 10^{-5}$ (in units of π/a_{wire}).

Fig. 5.1 presents the calculated zero-temperature ballistic conductance G in units of the quantum conductance $G_o = 2e^2/h$ for several different diameters of $\langle 110 \rangle$ -oriented Si NWs. As we discuss in Ch. 3, the band edge energies are aligned with respect to those of bulk Si. With increasing diameter, both the band gap energies and the spacing between the subbands decrease so that for a fixed Fermi energy the conductance is higher for the larger diameter NW, as would also be the case classically.

In the inset of Fig. 5.1, we give the electron and hole effective masses at the band edges in units of free electron mass m_o . Recalling our discussions about the indirect band gap of $\langle 110 \rangle$ Si NWs from Ch. 3, we note that the VB edge is located at Γ -point, whereas the CB edge is at an off- Γ -point. The corresponding effective masses are calculated at those band edge points. As seen in the figure, despite the energy shift, the curvature of band structure at the band edges remains the same so that the effective mass values do not alter. As a benchmarking, the calculated

effective mass values [$m_e \approx 0.57 m_o$ (off- Γ) and $m_h \approx 0.14 m_o$ (at Γ)] and their diameter independent characteristics are consistent with the H-passivated Si NW results [5, 83].

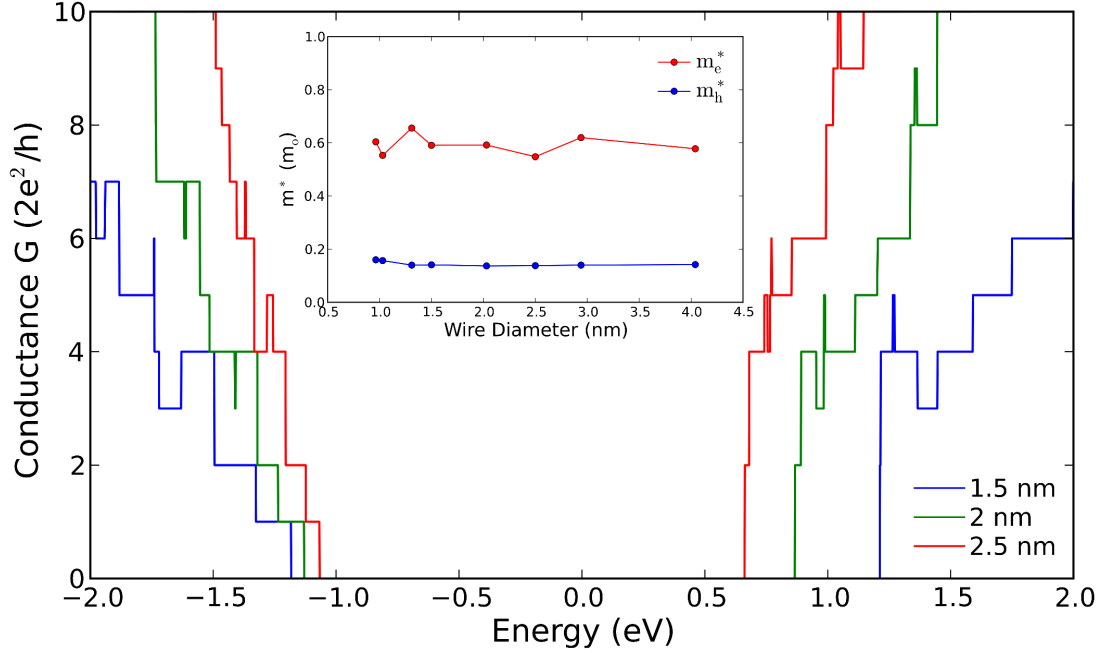


Figure 5.1: Zero-temperature ballistic conductance for 1.5 nm, 2 nm and 2.5 nm diameter $\langle 110 \rangle$ -aligned embedded Si NWs. In the inset, the band edge electron and hole effective masses are given for various diameters in the units of free electron mass m_o .

In Fig. 5.2, employing Eq. (4.49) with Eq. (4.50), we present the temperature dependence of ballistic conductance for the $\langle 110 \rangle$ -aligned Si NW of diameter of 2 nm. As a reminder, even though this is a finite-temperature calculation, it is in the ballistic transport regime, i.e., temperature dependent scattering mechanisms, namely phonons, do not degrade the conductance. Within this picture the sole effect of temperature is to smear out the sharp steps of zero-temperature conductance. As Eq. (4.43) indicates the smearing originates from the energy averaging of Fermi-Dirac distribution functions characterizing the injected carriers from the leads (reservoirs). The same finite-temperature behavior was reported by Bagwell and Orlando within the Landauer formula by engaging an energy convolution of Fermi-Dirac distribution functions [169].

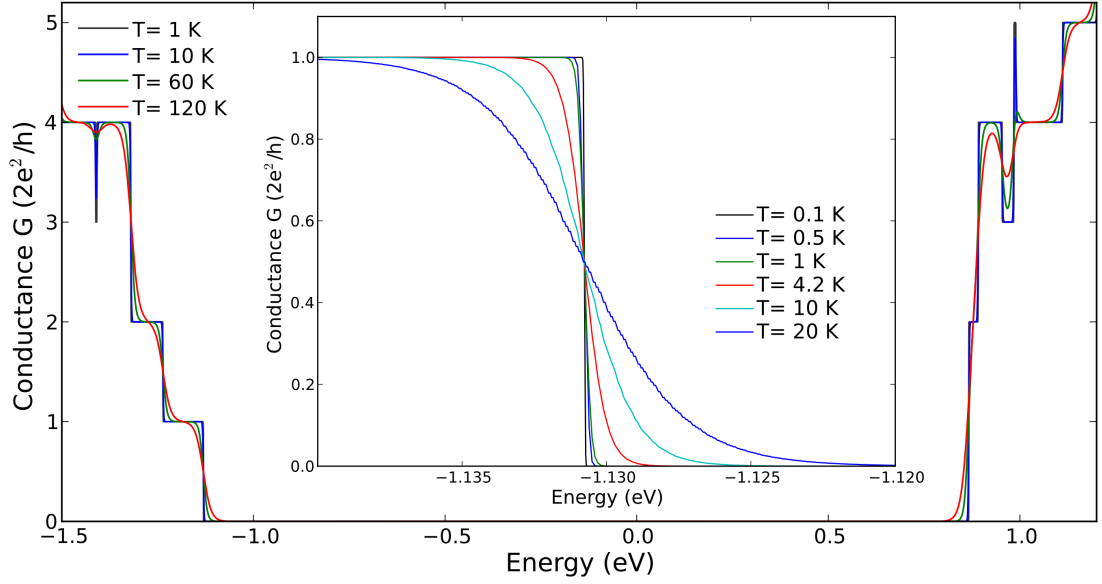


Figure 5.2: Finite temperature *ballistic* conductance of the $\langle 110 \rangle$ -aligned Si NW of diameter of 2 nm. In the inset, we focus on the VB edge for a variety of low-temperature values to indicate the smearing effect of temperature.

More investigations can be done for the transport features of single Si NWs, however, as we review in Ch. 1, the comprehensive studies have already been undertaken by many groups [14]. Thus, along the main spirit of our work dedicated to exploring the physics of more complex structures, after this short benchmarking, in the proceeding sections, we concentrate on them.

5.2 Carrier localization characteristics of NW Networks

About the band gap characteristics of NWNs, we had some observations in Ch. 3. These are mainly: (i) there is a reduction in the main band gap as we go from single NWs to crossings of them (see Sec.3.2). Within the reign of quantum confinement, the amount of the reduction depends on the numbers and relative diameters of the crossing NWs, (ii) the band gap reduction arises largely from

the shift of CB edge whereas the VB edge shifts very slightly (see Sec. 3.3 and Fig. 3.9).

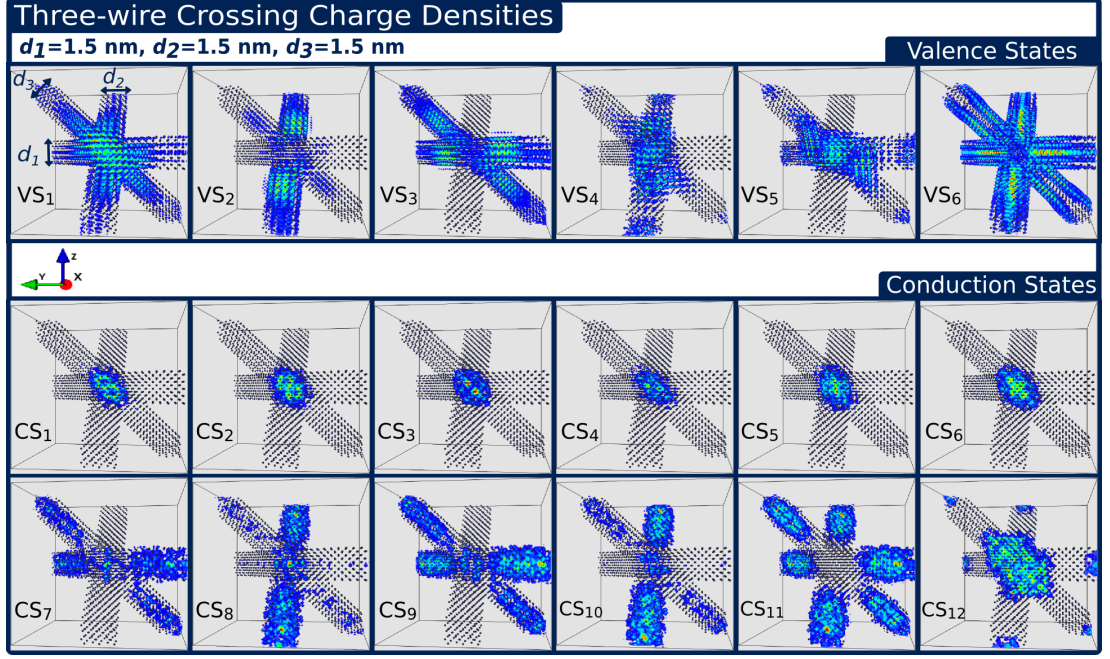


Figure 5.3: Isosurfaces for charge densities corresponding to the first six/twelve states below/above the valence/conduction band edges for the three-wire crossing with wire orientations along $\langle 110 \rangle$ directions and diameters of all 1.5 nm. The isosurfaces enclose densities from 100% to 10% of their respective maxima.

To elucidate the underlying physics of those outcomes, we consider some low-lying VB and CB wave functions of NWNs. In Fig. 5.3, we show the isosurfaces of carrier densities (wave function modulus squares) for the first six hole and twelve electron states below the VB edge and above the CB edge, respectively, for a three-wire crossing of equal wire diameters of all 1.5 nm. As seen the first six CB states are quite localized, whereas the VB states have a more extended state characteristic. Starting from the seventh one, CB states also starts to spread out over the network. Although the density isosurfaces give a first impression about the behaviors of carriers, these are not quantitative enough.

In order to develop a quantitative understanding on the carrier localizations, we shall exploit the ballistic transport calculations. Fig. 5.3 illustrates that the

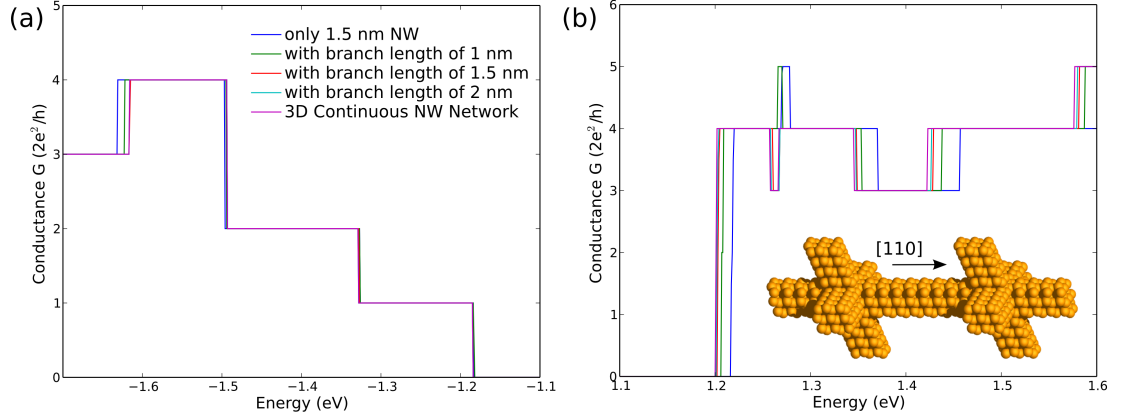


Figure 5.4: Calculated ballistic conductance around (a) VB and (b) CB edges for several structures such that: first the single Si NW of diameter of 1.5 nm is considered, then the branches are introduced on the NW (see the inset illustration, NW is continuous along the $[110]$ direction, the truncated branches are in the other $\langle 110 \rangle$ directions). By elongating branch lengths, the branching NWs are interconnected with the neighboring supercell images to build up a continuous network.

low-lying six CB edge states have a strong localization behavior. Thus, we can expect that those states will not contribute to the conduction. Let us examine the behavior from transport perspective.

As we discuss extensively in Chs. 2 and 4, we can compute the electronic structure and ballistic transport of nanostructures by following two approaches: (A1) We can employ a 2D planar $\vec{k}_\perp$ -grid approach where the planar $\vec{k}_\perp$ -grid is shifted by $\vec{k}_\parallel$ to scan the first BZ. Solving the separated eigenvalue problems at definite $\vec{k}_\parallel$ values, the proper dispersion relation $E_{n,k_\parallel} = E_n(k_\parallel)$ can be extracted. Then, importing the electronic structure results into Eq. (4.51), one can calculate the ballistic transport. (A2) Alternatively, we can exploit a 3D k -grid approach in which we do not separate the eigenvalue problem into definite $\vec{k}_\parallel$ ones, but solve it in one shot. This approach maps all the $E_{n,k_\parallel}$ values to $E_{n,k_\parallel=0} = E_{n,\Gamma}$, without discriminating the $k_\parallel$ values. Accordingly, we can not use Eq. (4.51) for the transport calculations, but instead, we need to utilize Eq. (4.42).

Regarding the single NWs, these two approaches end up with the same electronic structure and ballistic transport results. Nevertheless, when we consider

NWNs or other complex structures, the outcomes of those two methods deviate. All the energetics results represented in Ch. 3 are obtained via employing A2 approach. Let us now look for the findings of A1 approach.

Fig. 5.4 illustrates the result of this approach. Here, we systematically go from a single NW to a NWN such that first we consider a single NW of diameter of 1.5 nm and compute the ballistic conductance through its axial direction. Then, we add truncated branches to the NW. The inset of the figure illustrates a branched NW. We elongate the branch lengths progressively, till the images of neighboring supercells touch each other such that the branches interconnect to continuous NWNs (resulting network is same as Fig. 3.6(d) with NWs of equal diameters). In the figure, the conductance of the single NW is compared with the conductances of two branched NWs, of branch lengths of 1 nm and 2 nm, and with the continuous NWN, respectively. To briefly explain the calculation approach (A1), in these calculations we apply our single NW treatment to the branched ones and NWN. That is, we calculate the electronic structure along the axis of the original unbranched NW and then feed the transport computations with the band dispersion result. Henceforth, we obtain the ballistic transport of branched NWs and NWN through a specific constituent crossing NW (original unbranched NW in this case).

From our electronic structure results of Ch. 3 (all obtained via A2 approach), we know that the band gap values reduce with the increasing number of crossing wires (see Table 3.2) and we further know that the change indeed mostly originates from the shift of CB edge, whereas the VB edge shifts very slightly. (see Fig. 3.9). In striking contrast, Fig. 5.4 illustrates that (basing on A1 treatment) the ballistic transport edges are virtually fixed. Hence, this observation reveals that the low-lying CB edge states of NWN (see Fig. 5.3) are localized and so that do not contribute to the conductance.¹

To clarify localization behaviors further, in Fig. 5.5, we take the full advantage of our various KG-formulations. The power of KG-formula lies on Eq. (4.42) more

¹We note that the conventional word usage is misleading in this context. Though the name of the band edge is conduction band edge, it is actually not conducting, but rather a localized state. Alternatively, one can call them as electron states.

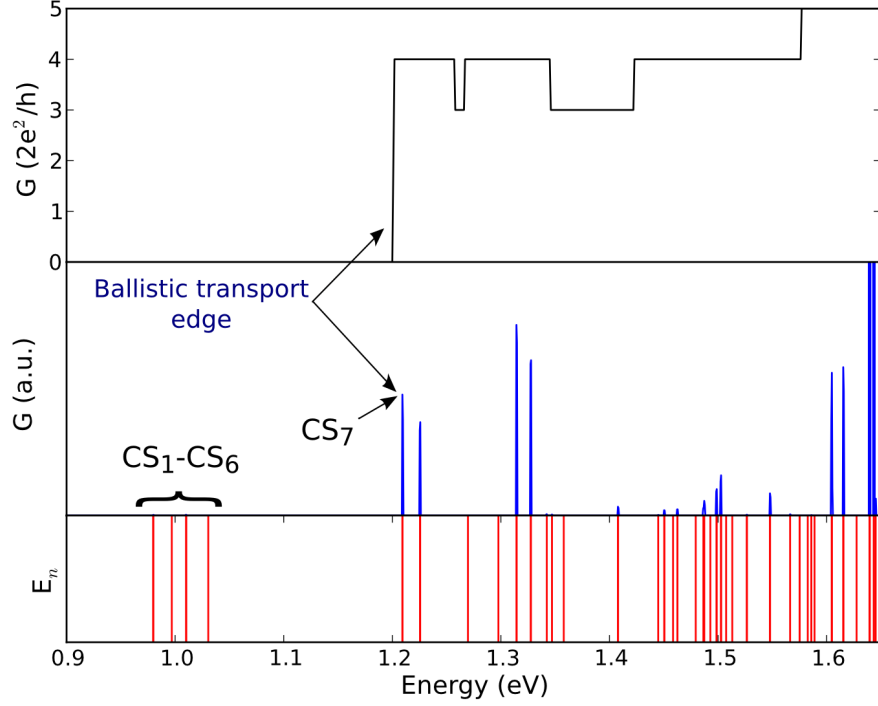


Figure 5.5: The calculated ballistic electron conductances and energy spectrum of a 3D NWN of equal wire diameters of all 1.5 nm (same as the network of Fig. 5.4). On top panel, the conductance through the 1D channel of [110] NW is calculated via A1 approach. In the middle panel, within A2 approach, the network is treated with a 3D k-grid, then the transport along the [110] direction is computed. In the bottom panel, the energy spectrum corresponding to middle panel is given.

than Eq. (4.51). Actually, the form of Eq. (4.51) is seemingly superfluous, since it eventually simplifies to the form of Eq. (4.53) and our derivation seems redundant. However, we note that when Eq. (4.53) is employed, it naively tells that if there is a state at a specific Fermi energy, then it has a contribution of G_o to the conductance. On the other hand, KG-formula sets that although there is a state at this energy, depending on its momentum matrix element, it may or may not be conducting. Hence, Eq. (4.42) has the ability to point out the conduction of each individual state.

Before interpreting Fig. 5.5, we would like to remind an important implementation detail of A1 approach. As we point out in Sec. 4.4, to obtain the ideal

conductance steps of 1D transport, we first perform the electronic structure computation with about 100 number of $k_{\parallel}$ -points sampling the first BZ. Then, we further interpolate the energy dispersion to about 3000-4000 points. Once the dispersion is so dense, the KG-formula succeeds to display ideal conduction steps. Within 3D k-grid-based A2 approach, such a dense k-gridding is computationally intractable, and moreover, since all the states are mapped to Γ , into nanocrystal-like energy spectrum, the interpolation is not possible. Due to these factors, when A2 is applied to the transport calculations, the conduction results reveal sparse and discrete Dirac delta-like conduction peaks. Ideally, increasing the number of points in 3D k-grid, those peaks will evolve to continuous conduction steps. In App. B, we demonstrate the transition from peaks to ideal conduction steps and vice versa, by considering the toy model of hard-wall NWs.

Now turning back to Fig. 5.5, on the top panel the conductance result of A1 approach is displayed. Treating the NWN as a 1D channel through one of its constituent NW, this approach calculates the conductance of NW-like dispersive states. Accordingly, the conduction results are NW-like conductance steps. In the middle panel, A2-based conduction values are presented. Since the peak values of Dirac delta functions depend on the broadening parameters, we give the conductance values in arbitrary units (a.u.).² In the bottom panel, A2-based energy spectrum is given. The figure clearly illustrates that the six low-lying CB edge states do not contribute the conductance, having a localized character. Both the A1 and A2 approaches indicate the same energy level as the ballistic transport edge. That is the energy level of CS_7 of Fig. 5.3 which is very close to the energy level of a single NW of diameter of 1.5 nm (as also indicated by Fig. 5.4). Once the Fermi energy reaches to that level, the NW channels become open to the transport. We note that there are also localized states above the ballistic transport edge.

²Eq. (4.42) is written for the conductivity σ . A geometry dependent multiplication factor relates it with the conductance G . Here, we express the conductance values to have a general consistence among the figures. At all, we give the conductance in arbitrary units (a.u.) to defuse the broadening dependent Dirac delta function contributions. The implementation of Eq. (4.42) include two broadening parameters: γ_F to find the roots of the Dirac delta functions, $|E_F - E_l| < \gamma_F$ and γ_B to broaden the Dirac delta functions either by applying Gaussian or Lorentzian broadening. In the figures, to isolate the peak per state, we employ $\gamma_B = 2$ meV and $\gamma_F = 1$ meV.

To sum up, we can employ A1 and A2 approaches together to display a complete picture of localization-delocalization and transport characteristics of the NWN. 2D k-grid-based A1 approach catches only the NW-like dispersion and is blind to the localized states. However, 3D k-grid-based A2 approach catches both type of states. From the conduction results of these two methods, we can separate the localized states from the conducting ones and can define a ballistic transport edge.

Those results indicates that, the quantum interference effects play a prominent role at the crossing regions. Constructive interference of electron waves of different crossing NW channels lead to standing waves, i.e. to the localized-bound states at the crossings. In addition to interference effects, the uniform potential of the NW wall alters at the crossing regions, inducing a weak disorder in the system. The interplay of quantum interference effect and variation of the local potential profile stands as the cause of localized states. As a final remark, as we know from the single NW case, VB states respond very slightly to the confinement change. Inheriting that in the networks, the outstanding localization behavior does not reveal on the VB states.

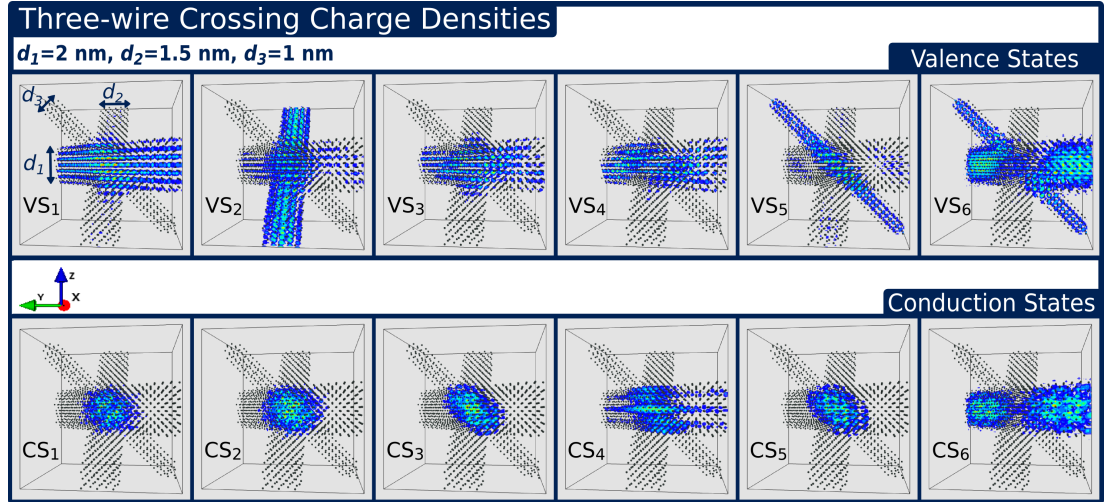


Figure 5.6: Isosurfaces for charge densities corresponding to the first six states below/above the valence/conduction band edges for the three-wire crossings with wire orientations along $\langle 110 \rangle$ directions and diameters of 1 nm, 1.5 nm, and 2 nm. The isosurfaces enclose densities from 100% to 10% of their respective maxima.

We recall our energetics result that the amount of the gap reduction (from single NWs to NW crossings, see Table 3.2) depends on the relative diameters of the crossing NWs, the widest NW dictating the band gap. To grasp the case of distinct diameters, in Fig. 5.6, we present the isosurfaces for charge densities of the three-wire crossing with diameters of 1 nm, 1.5 nm, and 2 nm. We observe that the VB states get further spread out, and some of the lowest CB states also delocalized, in particular, along the thickest NW. The band gap value of the crossing is quite close to gap value of single 2 nm NW (the former is not listed in Table 3.2 which is 1.92 eV, the latter is 1.99 eV as given in the table). In the light of aforementioned discussions, the very slight reduction comes from the a few localized CB states. Then the extended states through 2 nm NW follows. This indicates that the formation and energy of a bound state depends on the relative diameters of the NWs.

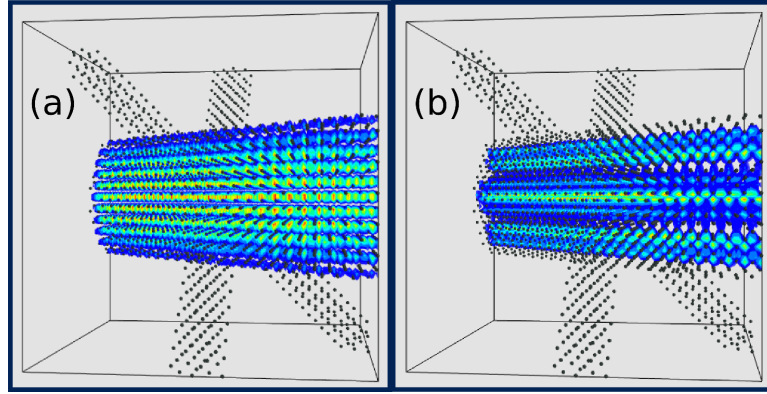


Figure 5.7: Isosurfaces for charge densities corresponding to the (a) highest VB and (b) lowest CB edge states for a $\langle 110 \rangle$ three-wire crossing with wire diameters of 1 nm, 1 nm, and 3 nm. The isosurfaces enclose densities from 100% to 10% of their respective maxima. Carriers densities extend through the widest crossing wire.

In Fig 5.7 charge density isosurfaces are given for the VB and CB edge states of a three-wire crossing with diameters of 1 nm, 1 nm, and 3 nm. As the difference among the diameters of crossing NWs becomes very large, the NWNs behave like isolated NW arrays with the thin wire branches ignored. The reasoning is same as the crossings of 1 nm, 1.5 nm and 2 nm NWs, but now since the energy levels of 1 nm NWs are very high with respect to band edge states of 3 nm NW,

the thin branches have no effect on the very low-lying states.

Our results and analysis given in Ch. 3, for the Si NWs and NWNs, are based on energetics. Apart from the deviation in the scaling exponent α , our atomistic approach is seemingly in harmony with the effective mass models both serving to the quantum confinement spirit. However, the major observation here is that the NWNs in their full assembly display interesting charge profiles that are inaccessible within an effective mass-based continuum model. An atomistic treatment is essential to capture the intricate pattern of localized versus extended natures of low-lying states. These characteristics of wave functions lead us to suggest that electronic structure of networks exhibits tails of localized states at each band edge with more and stronger localized states at the CB edge, i.e., holes can migrate easier through a network than electrons. The occurrence of localized states can be of some concern for applications of networks such as in photovoltaics. The predictions of the presented calculations can be taken into consideration in the design of photovoltaic cells based on networks with optimum charge carrier separation.

5.3 Comparison of Nanowire Networks with Branched Nanocrystals and Nanowires

Equipped with the behaviors of band edge energies and carrier localizations, we can compare the band gap values of branched nanostructures and continuous networks. In Fig. 5.8, the first nanostructure is a nanocrystal with 6 branches of equal length, which is a crossing of three $\langle 110 \rangle$ -oriented 3 nm long nanorods with diameters of 1 nm. In the figure for better illustration the branch lengths are exaggerated. In the second nanostructure, i.e. branched NW, the branched nanocrystals are interconnected along one direction so that a NW with 1 nm diameter is continuous along one direction but has truncated branches along the other two directions. In the third nanostructure, the branched NWs are interconnected also along the truncated directions so that three-wire crossings build up a 3D continuous network (which is identical to Fig. 3.6(d) with NWs of

equal diameters).

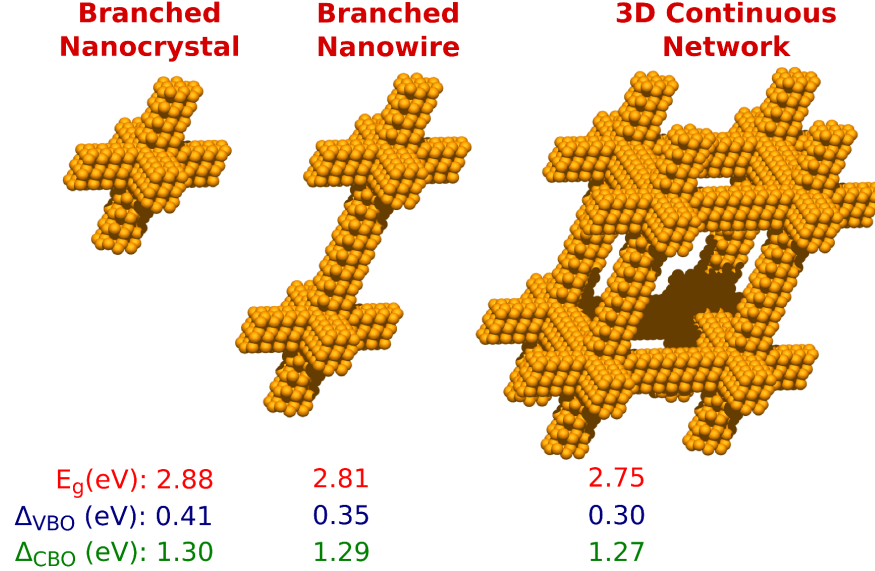


Figure 5.8: Comparison of band gap values (E_g), as well as valence (Δ_{VBO}) and conduction (Δ_{CBO}) band offsets with respect to bulk Si band edges for a branched nanocrystal, branched NW and continuous 3D network. The wire and rod alignments are along $\langle 110 \rangle$ directions.

Despite the marked discrepancy among the structures, intriguingly, the corresponding band gap differences are only marginal (listed in Fig. 5.8). This can be reconciled by invoking localization, and band edge energetics. First, we recall that it is the valence states, which mainly spread throughout the nanostructure, “feeling” the extension of the system, whereas the lowest conduction states localizes to a very narrow region of crossing (considering Fig. 5.3). This furthermore combines with the fact that the VB edge is relatively insensitive to the structural changes (see Fig. 3.9 and discussion therein). Henceforth, we infer that our band gap results obtained for networks will also apply to branched nanocrystals and branched NWs.

5.4 Kinked Nanowires

The advancements in the ability to control the growth of NWs pave the way to fabricate new class of complex shaped nanostructures, including T- [170] and Y-branched [171], kinked [172] and L-shaped [172, 166] NWs. Displaying intriguing quantum interference effects these structures are candidates for complex quantum waveguide structures as building blocks of quantum network devices [173].

The kinked NWs (KNWs), by themselves, are quite rich structures regarding their geometries. One can consider U-, V-, and W-shaped KNWs [166, 167, 168]. Here, to demonstrate the ability of our computational implementation, we consider U-shaped KNWs. Fig. 5.9 illustrates the schematic view of a U-shaped KNW. The blue and green segments are aligned in the $[110]$ direction, the two red segments, aligning along the $[100]$ direction, connecting them. Even only for the U-shaped KNWs, one can benefit from various opportunities for the electronic structure engineering by varying the diameter and lengths of NW segments or by changing the alignment direction.

The KNWs are *mega-structures* of this work, in the sense that the computational supercells contain 10000-15000 number of atoms, including the embedding medium. To reduce computational load, we consider only the electron states. As we see in the case of NWNs, the behavior of electron states is more drastic with the change of system geometry.

Fig. 5.10 presents the analog of Fig. 5.5 for the KNWs. On the top panel, we treat the KNW via A1 approach, i.e., scanning the BZ with 2D k-grids, we identify the NW-like conducting states. This approach captures the conductance steps, i.e., NW-like dispersive states, starting from a ballistic transport edge at around 1.77 eV. On the middle panel, we present the conductance values calculated by A2 approach, which is zoomed in the inset of top panel. On the bottom panel the energy spectrum corresponding to middle panel is given.³ We again observe some conduction peaks. Note that the onset of these peaks is very close to the ballistic

³To give a consistent picture with the NWN calculations, we give the energy levels as “they come out”, alternatively, the energy levels can be presented in reference to bulk Si CB edge, that can be done by extracting the value of 0.22 eV from those energies.

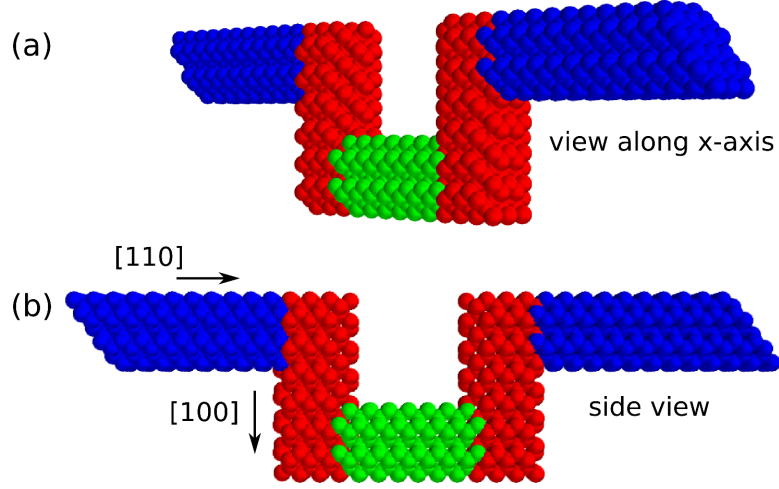


Figure 5.9: A representative kinked NW illustrated from two aspects. The blue and green segments are along the $[110]$ direction, whereas the red ones are along $[100]$ direction. Regarding also the supercell periodicity along the kinked NW, the shape can be altered by changing: (i) total length of blue segments, (ii) length of red segments, (iii) length of green segment. The supercell contains 1532 Si and in total 13328 atoms.

transport edge indicated by top panel. The slight differences in the transport edges, predicted by A1 and A2 approaches, most likely originate from the k-grid convergence performances of these two gridings.

This figure indicates three types of states regarding the relative values of their conduction peaks: (S1) totally localized-bound states, not contributing to the conductance, (S2) quasi-bound states, having low conductance peaks, (S3) NW-like extended states which have higher conductance peaks and also lies beyond the ballistic transport edge as indicated by top panel of Fig. 5.10.

Planar k-grid approach (A1) is not able to capture S1 and S2 states, but identifies the S3 states which have a full 1D dispersion and can contribute to the conductance with G_o steps. S2 states have a lower conductance, at first glance, they seem to exhibit a different transport mechanism. S1 states are corresponding to the localization states which originate from the quantum interference effect. The band gap is determined by a low lying bound state [we call it as the lowest unoccupied molecular orbit (LUMO)], the ballistic transport edge stands at a

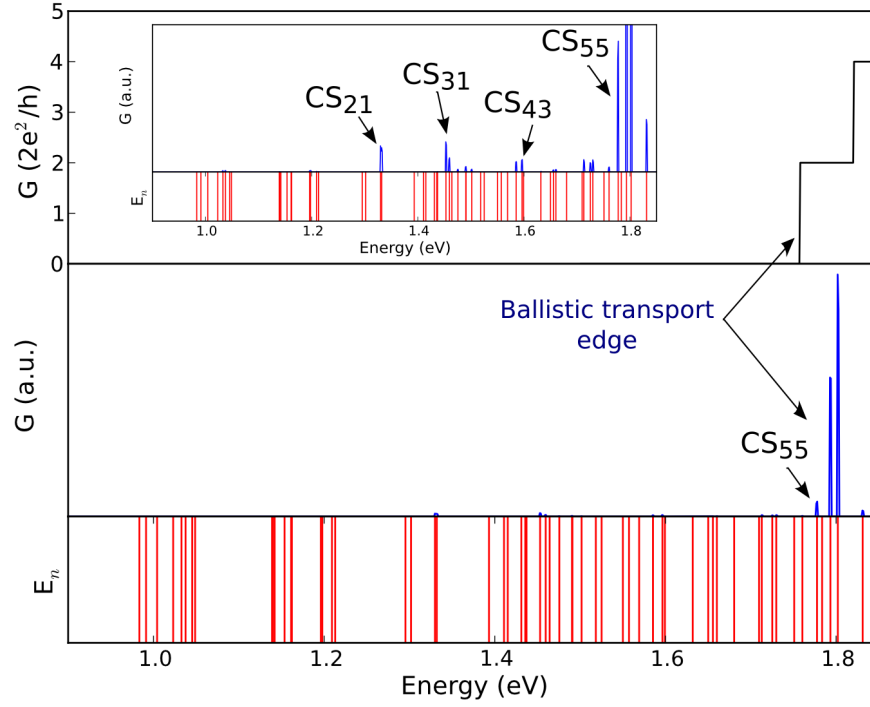


Figure 5.10: The calculated ballistic electron conductances and energy spectrum of a KNW of all the segments have diameter of 1.5 nm. On top panel, the A1 approach is exploited to extract the NW-like extended states and their corresponding conductance steps. In the middle panel, within A2 approach, the KNW is treated with a 3D k-grid, then the transport along the [110] direction is computed. In the bottom panel, the energy spectrum corresponding to middle panel is given.

higher energy level. We note that the value of the edge (around 1.77 eV) is higher than the band edges of both [110] (1.21 eV) and [100]-aligned (1.32 eV) single NWs (see Note 3).

In Fig. 5.11, we illustrate the isosurfaces of carrier densities for several electron states. The isosurface of first 12 states (CS₁-CS₁₂) are belonging to S1-type states, indicating localized characteristics. The representative states CS₂₁, CS₃₁, and CS₄₃ are S2-type also marked on Fig. 5.10. As see in Fig. 5.11, their isosurfaces also indicate an extended behavior. Rest of the states given in Fig. 5.11 are lying at or beyond the ballistic transport edge, exhibiting NW-like extensions.

In Fig 5.12, we indicate the energetics of LUMO states of three different shape

KNWs. In those structures, the length of the [100]-aligned segment is increased so that standing waves have a larger volume to occupy. As expected from the quantum confinement, with increasing length of [100] segment the LUMO energy decreases.

Our findings on the transport properties reveal that the kinks and crossings of NWs display a rich localization behavior such that the ballistic transport edges set apart the extended states from the localized-bound ones. Though the band gaps are imposed by the latter ones, by localized character they do not contribute to the conductance. Conductance of these nanostructures undergoes a sharp transition once the Fermi level reaches to the ballistic transport edge, as of the transport channels through a specific crossing NW or through the KNW are opened up.

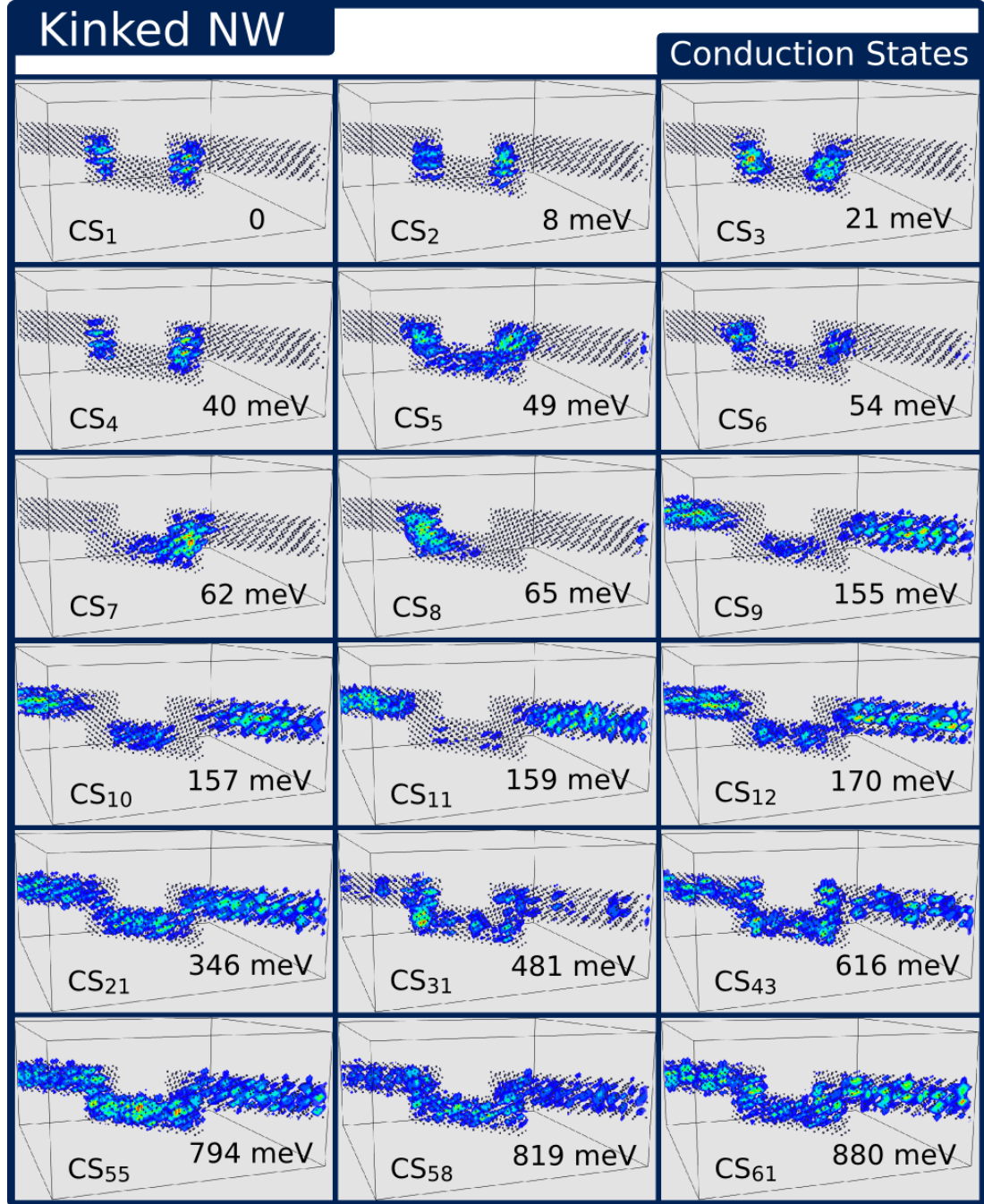


Figure 5.11: Isosurfaces for charge densities corresponding to several conduction states (CS) of a KNW. The isosurfaces enclose densities from 100% to 10% of their respective maxima.

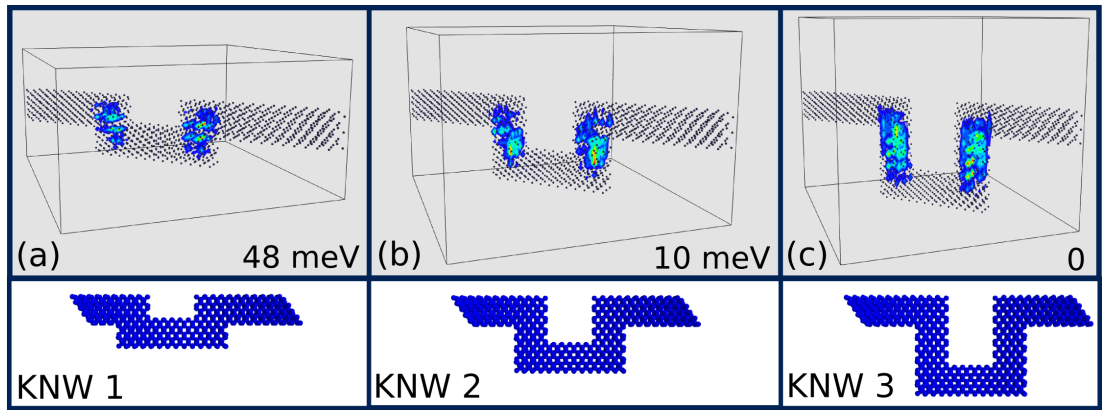


Figure 5.12: Isosurfaces for charge densities of LUMOs of three different shape KNWs. The energy levels of the states are also given in reference to lowest of them. As expected from the quantum confinement, with increasing volume of $[100]$ segment the energy value of LUMO decreases. The isosurfaces enclose densities from 100% to 10% of their respective maxima.

Chapter 6

Conclusion and Outlook

We have systematically investigated the electronic properties of Si NW-based complex structures by providing a large-scale atomistic insight into the band gaps, band alignments, carrier localization behaviors, and ballistic transport features.

The electronic structures are computed via the LCBB method within an atomistic pseudopotential framework. All the nanostructures considered are embedded into an oxide matrix to provide the surface passivation. Extensive information is given for the formalism of LCBB method, underlining the critical implementation details such as k-grid construction and sampling. The employed pseudopotential scheme, together with the corresponding parameters, are presented. The computational considerations as well as the convergence performances are documented.

During the progress of this work, a great effort and time has been spent to the computational implementation of LCBB method. The method has several advantages including enabling the computation of large-scale atomic systems, reliable energetic outputs, and low computational run time. We have broadly exploited all those advantages in this work. Nevertheless, despite the capabilities, during our in-house implementation, we have been faced with several obstacles such as the proper surface passivation scheme, filtration of interface states, k-point sampling and special care for the energy dispersion relations. Hence, besides the understanding of physics of nanostructures, we bequeath some to the literature

of this less employed method.

As a benchmark and start up, we investigated the embedded single Si NWs, considering the variation of electronic band gap and band edge alignments as a function of diameter for several important high-symmetry orientations of Si NWs. We observed that the valence band offset at the Si NW/SiO₂ interface is rather close to the bulk interface whereas the conduction band offset significantly shifts with decreasing wire diameter. After establishing the single-wire case, we extended our consideration to the main subject of this work of two- and three-dimensional Si NW networks (NWNs). With a comprehensive analysis, we proposed an expression to estimate the band gap values of network systems as a function of crossing wire diameters. The form of the expression should, in principle hold for other materials as well, to assist the band gap engineering of NWNs. The expression can also be exploited to calculate the valence and conduction band alignments of NWNs in reference to bulk Si. As expected from the findings of single NWs, a wire-crossing has corresponding band gap value mainly due to the shift of conduction band edge whereas the valence band edge energy is quite close to that of bulk Si.

To gain more insight to the calculated band gap values, we have considered the isosurfaces of charge densities for low-lying band edge states. We showed that the valence states are spread through the branches whereas the conduction states can be strongly localized at the intercrossing regions, depending on the relative diameters of crossing NWs. Moreover, we pointed out that the band gap results provided here for Si NWNs are also valid for the branched Si nanocrystals and NWs owing to interplay of band edge shifting energetics and localization characteristics of carriers at the crossings. We address the localization behavior in more detail by studying the quantum ballistic transport features of those nanostructures at the linear response regime within the Kubo-Greenwood formalism. We uncover intriguing quantum interference effects at the crossings and kinks of NWs, leading to the localized-bound states.

This study is intended to be a single-particle level exploratory scrutiny of Si NWs-based complex structures for a restricted energy range around the band

gap. Neither the surface reconstruction nor the structure relaxation are included in this study. This approach is adopted to investigate the sole effect of size and shape on the electronic structure and transport features. Equally-important aspects such as the analysis of interface states [87], many-body effects [174], exciton transport [6], and the scattering mechanisms such as surface roughness [65], impurities [88], and phonon processes [63] as well as strain impacts [80] are left out of the scope of this work. This study can be expanded in any of those dimensions. In particular, the calculations given in this work are for relatively large diameters. A complimentary follow-up could be a first-principles investigation for smaller-diameter networks to shed light especially on surface chemistry and strain effects.

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Appendix A

Momentum Matrix Elements within LCBB

A.1 3D k-grid General Case

The momentum matrix elements $\langle l|\vec{P}|l'\rangle$ between two states l and l' can be expressed in the position representation using $\vec{P} = -i\hbar\vec{\nabla}$ and inserting $\hat{I} = \int d^3r|\vec{r}\rangle\langle\vec{r}|$,

$$\langle l|\vec{P}|l'\rangle = \int_V d^3r \Psi_l^*(\vec{r})(-i\hbar\vec{\nabla})\Psi_{l'}(\vec{r}), \quad (\text{A.1})$$

where $V = N\Omega_o$ is the volume of the supercell. Recalling LCBB expanded nanostructure wave functions Eq. (2.5)

$$\Psi_j(\vec{r}) = \sum_{n,\vec{k},\sigma} C_{n,\vec{k},j}^\sigma \sum_{\vec{G}} \left[\frac{1}{\sqrt{V}} B_{n\vec{k}}^\sigma(\vec{G}) e^{i(\vec{k}+\vec{G})\cdot\vec{r}} \right], \quad (\text{A.2})$$

and inserting into Eq. (A.1) we get

$$\begin{aligned} \langle l|\vec{P}|l'\rangle = \int_V d^3r \frac{1}{N\Omega_o} \sum_{\substack{n,\vec{k},\sigma,\vec{G} \\ n',\vec{k}',\sigma',\vec{G}'}} C_{n,\vec{k},l}^{\sigma*} B_{n\vec{k}}^\sigma(\vec{G})^* \hbar(\vec{k}' + \vec{G}') C_{n',\vec{k}',l'}^{\sigma'} B_{n'\vec{k}'}^{\sigma'}(\vec{G}') \\ \times e^{i(\vec{k}'+\vec{G}'-\vec{k}-\vec{G})\cdot\vec{r}}. \end{aligned} \quad (\text{A.3})$$

Again using $\vec{r} = \vec{R}_j + \vec{r}_p$ and $\int_V d^3r \rightarrow \sum_{j=1}^N \int_{\Omega_o} d^3r_p$ we write

$$\frac{1}{N\Omega_o} \int_V e^{i(\vec{k}' + \vec{G}' - \vec{k} - \vec{G}) \cdot \vec{r}} d^3r = \frac{1}{N} \sum_{j=1}^N e^{i(\vec{k}' + \vec{G}' - \vec{k} - \vec{G}) \cdot \vec{R}_j} \frac{1}{\Omega_o} \int_{\Omega_o} e^{i(\vec{k}' + \vec{G}' - \vec{k} - \vec{G}) \cdot \vec{r}_p} d^3r_p, \quad (\text{A.4})$$

employing $\frac{1}{N} \sum_{j=1}^N e^{i(\vec{k} - \vec{k}') \cdot \vec{R}_j} = \delta_{\vec{k}, \vec{k}'}$ and $\frac{1}{\Omega_o} \int_{\Omega_o} d^3r_p e^{i(\vec{G} - \vec{G}') \cdot \vec{r}_p} = \delta_{\vec{G}, \vec{G}'}$, also since $e^{i(\vec{G} - \vec{G}') \cdot \vec{R}_j} = 1$ we get the compact expression for the momentum matrix elements

$$\langle l | \vec{P} | l' \rangle = \sum_{\substack{n, \vec{k}, \sigma \\ n', \vec{k}', \sigma', \vec{G}}} C_{n, \vec{k}, l}^{\sigma*} B_{n\vec{k}}^{\sigma}(\vec{G})^* \hbar(\vec{k} + \vec{G}) C_{n', \vec{k}', l'}^{\sigma'} B_{n'\vec{k}'}^{\sigma'}(\vec{G}) \delta_{\vec{k}, \vec{k}'}, \quad (\text{A.5})$$

A.2 2D k-grid Nanowire Case

First, we rewrite the nanowire wavefunction from Eq. (2.19)

$$\Psi_{j, \vec{k}_{\parallel}}(\vec{r}) = \frac{1}{\sqrt{V}} \sum_{n, \vec{k}_{\perp}, \sigma} C_{n, \vec{k}_{\perp}, \vec{k}_{\parallel}, j}^{\sigma} \sum_{\vec{G}} B_{n\vec{k}}^{\sigma}(\vec{G}) e^{i(\vec{k}_{\perp} + \vec{G}_{\perp}) \cdot \vec{r}_{\perp}} e^{i(k_{\parallel} + G_{\parallel})r_{\parallel}}. \quad (\text{A.6})$$

We can drop the vector sign of $\vec{k}_{\parallel}$ since it is in the direction of nanowire BZ obviously. Since we are looking for definite $k_{\parallel}$, we also change the sum over $\vec{k}$ to sum over only $\vec{k}_{\perp}$.

$$\begin{aligned} \langle l k_{\parallel} | \vec{P} | l' k'_{\parallel} \rangle &= \int_V d^3r \frac{1}{N_{\perp} \Omega_o} \sum_{\substack{n, \vec{k}_{\perp}, \sigma, \vec{G} \\ n', \vec{k}'_{\perp}, \sigma', \vec{G}'}} C_{n, \vec{k}_{\perp}, l}^{\sigma*} B_{n\vec{k}}^{\sigma}(\vec{G})^* \hbar(\vec{k}' + \vec{G}') C_{n', \vec{k}'_{\perp}, l'}^{\sigma'} \\ &\quad \times B_{n'\vec{k}'}^{\sigma'}(\vec{G}') e^{i(\vec{k}'_{\perp} - \vec{k}_{\perp} + \vec{G}'_{\perp} - \vec{G}_{\perp}) \cdot \vec{r}_{\perp}} e^{i(k'_{\parallel} - k_{\parallel} + G'_{\parallel} - G_{\parallel})r_{\parallel}}. \end{aligned} \quad (\text{A.7})$$

Again using $\vec{r} = \vec{R}_{\perp, l} + \vec{r}_{\perp, p} + \vec{r}_{\parallel, p}$ so that $\vec{r}_{\perp} = \vec{R}_{\perp, l} + \vec{r}_{\perp, p}$ and $\vec{r}_{\parallel} = \vec{r}_{\parallel, p}$ Also considering $\int_V d^3r \rightarrow \sum_{l=1}^{N_{\perp}} \int_{A_o} d^2r_{\perp, p} \int_{L_o} dr_{\parallel, p}$, we obtain the term which needs to be treated

$$\frac{1}{N_{\perp}} \sum_{l=1}^{N_{\perp}} e^{i(\vec{k}'_{\perp} - \vec{k}_{\perp}) \cdot \vec{R}_{\perp, l}} \frac{1}{A_o} \int_{A_o} d^2r_{\perp, p} e^{i(\vec{k}'_{\perp} - \vec{k}_{\perp} + \vec{G}'_{\perp} - \vec{G}_{\perp}) \cdot \vec{r}_{\perp, p}} \quad (\text{A.8})$$

$$\times \frac{1}{L_o} \int_{L_o} dr_{\parallel, p} e^{i(k'_{\parallel} - k_{\parallel} + G'_{\parallel} - G_{\parallel})r_{\parallel, p}}. \quad (\text{A.9})$$

To simplify this expression we exploit the identities that $e^{i(\vec{G}_\perp - \vec{G}'_\perp) \cdot \vec{R}_{\perp,l}} = 1$, $\frac{1}{N_\perp} \sum_{l=1}^{N_\perp} e^{i(\vec{k}_\perp - \vec{k}'_\perp) \cdot \vec{R}_{\perp,l}} = \delta_{\vec{k}_\perp, \vec{k}'_\perp}$, $\frac{1}{A_o} \int_{A_o} d^2 r_{\perp,p} e^{i(\vec{G}_\perp - \vec{G}'_\perp) \cdot \vec{r}_{\perp,p}} = \delta_{\vec{G}_\perp, \vec{G}'_\perp}$. Since we have periodic boundary conditions in LCBB method, the length of the nanowire is ideally infinite. Then the last integration term can be written as

$$\int_{-\infty}^{+\infty} e^{i(k'_\parallel + G'_\parallel - k_\parallel - G_\parallel)r_{p_\parallel}} dr_{p_\parallel} = \delta(k'_\parallel + G'_\parallel - k_\parallel - G_\parallel). \quad (\text{A.10})$$

Here, $G_\parallel - G'_\parallel = G''_\parallel$ where $G''_\parallel$ is another reciprocal lattice vector. Regarding our k-grid construction that k-points are sampled from a volume enclosed by the planes which are perpendicular bisectors of the reciprocal lattice primitive vectors centered around the Γ , the Dirac delta function will be non-zero if and only if $G''_\parallel = 0$ and $k_\parallel = k'_\parallel$. Hence, we can write that $\delta(k'_\parallel + G'_\parallel - k_\parallel - G_\parallel) = \delta_{k_\parallel k'_\parallel} \delta_{G_\parallel G'_\parallel}$. Inserting back into Eq.(A.7), we obtain

$$\begin{aligned} \langle l k_\parallel | \vec{P} | l' k'_\parallel \rangle &= \delta_{k_\parallel k'_\parallel} \sum_{\substack{n, \vec{k}_\perp, \sigma \\ n', \vec{k}'_\perp, \sigma' \\ \vec{G}, \vec{G}'}} C_{n, \vec{k}_\perp, \vec{k}_\parallel, l}^{\sigma*} B_{n\vec{k}}^\sigma(\vec{G})^* \hbar(\vec{k}' + \vec{G}') C_{n', \vec{k}'_\perp, \vec{k}'_\parallel, l'}^{\sigma'} B_{n'\vec{k}'}^{\sigma'}(\vec{G}') \\ &\quad \times \delta_{\vec{k}_\perp, \vec{k}'_\perp} \delta_{\vec{G}_\perp, \vec{G}'_\perp} \delta_{G_\parallel G'_\parallel} \quad (\text{A.11}) \end{aligned}$$

Thanks to the Kronecker delta terms, this is indeed same as Eq. (A.5). The only difference is that now $\vec{k}$ should be a planar k-grid $\vec{k}_\perp$ centered at definite $\vec{k}_\parallel$.

Appendix B

Toy Model: Conductance of Hard-Wall NWs

For a rectangular nanowire of infinite potential walls, the wave functions have the form of

$$\langle \mathbf{r} | l \rangle = \psi_{n_x n_y n_z}(x, y, z) = \sqrt{\frac{4}{L_x L_y}} \sin\left(\frac{\pi n_x x}{L_x}\right) \sin\left(\frac{\pi n_y y}{L_y}\right) e^{i k_z z}, \quad (\text{B.1})$$

where $n_\alpha = 1, 2, 3, \dots$ and $\alpha = x$ and y . For a wire of infinite length, k_z is continuous whereas for a wire of length L_z , $k_z = \frac{2\pi n_z}{L_z}$ where $n_z = 0, \pm 1, \pm 2, \dots$. The energy spectrum of a nanowire consists of sub-bands with dispersion along the wire direction (z-direction for this case). Along the wire direction we assume that wire is “free” and the dynamical properties are expressed by the effective mass, m^* . The total energy of an eigenstate $\psi_{n_x n_y n_z}(x, y, z)$ is

$$E_{n_x n_y n_z} = E = \frac{\hbar^2}{2m^*} \left(\frac{\pi^2 n_x^2}{L_x^2} + \frac{\pi^2 n_y^2}{L_y^2} \right) + \frac{\hbar^2}{2m^*} \left(\frac{2\pi n_z}{L_z} \right)^2. \quad (\text{B.2})$$

The minimum energy in each of the sub-bands is the bottom of the band where n_z , so k_z , is zero

$$E_{n_x n_y 0} = \frac{\hbar^2 \pi^2}{2m^*} \left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} \right). \quad (\text{B.3})$$

We can evaluate the momentum matrix elements via the position representation $|\mathbf{r}\rangle$.

$$\langle l' | P_i | l \rangle = \int d\mathbf{r} \langle l' | \mathbf{r} \rangle \langle \mathbf{r} | P_i | l \rangle = \int d\mathbf{r} \langle l' | \mathbf{r} \rangle \left(-i\hbar \frac{\partial}{\partial x_i} \right) \langle \mathbf{r} | l \rangle, \quad (\text{B.4})$$

where we used the position representation of momentum operator, $P_i = -i\hbar \frac{\partial}{\partial x_i}$.

Performing the integration given in Eq. (B.4) with the wave functions given in Eq. (B.1), the momentum matrix elements along the wire direction are

$$\langle l' | P_z | l \rangle = \langle n'_x n'_y n'_z | P_z | n_x n_y n_z \rangle = \hbar \frac{2\pi n_z}{L_z} \delta_{n'_x n_x} \delta_{n'_y n_y} \delta_{n'_z n_z} = \hbar k_z \delta_{n'_x n_x} \delta_{n'_y n_y} \delta_{n'_z n_z}, \quad (\text{B.5})$$

and for the other two directions, which are perpendicular to the wire direction, the momentum matrix elements are zero. Thus, only the σ_{zz} entry of the conductivity tensor is non-zero, i.e. the conduction is only along the wire alignment direction. Inserting energy dispersion [Eq. (B.2)] and the momentum matrix elements [Eq. (B.5)] into Eq. (4.51), one get the zero-temperature dc-conductance of hard-wall NWs.

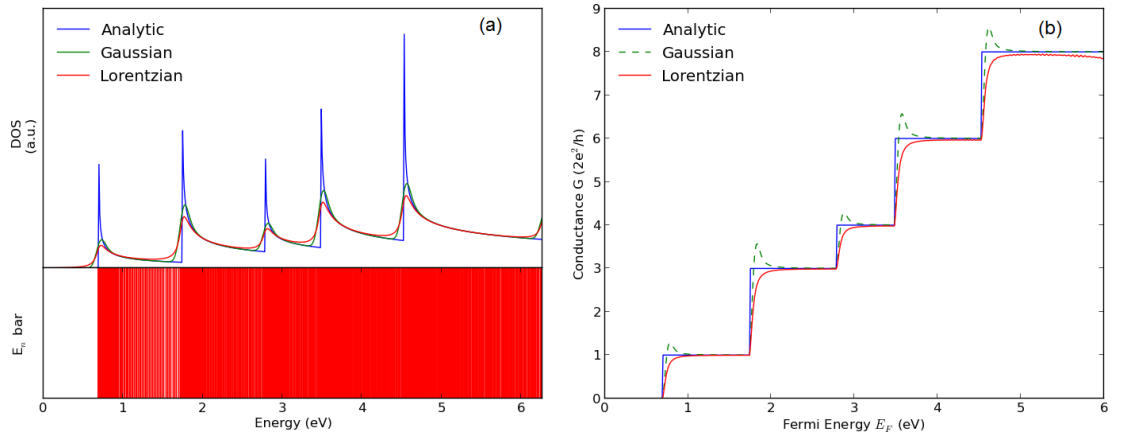


Figure B.1: (a) In the bottom panel, energy spectrum obtained by Eq. (B.2) for the nanowire of infinite potential walls and size of $L_x = 1$ nm and $L_y = 1$ nm. In the top panel, the corresponding DOS is calculated via Eq. (B.6). To approximate the analytic result, $L_z = 100$ nm and $N_z = 200$ are taken. (b) The zero-temperature dc-conductance of the NW in the units of $2e^2/h$. Analytic result is compared with the Gaussian and Lorentzian broadened density of states. The broadening parameter $\gamma = 0.05$ eV.

The DOS of NWs can be expressed either by the well-known analytical form or by considering the very definition of DOS as $g_{n_x n_y}(E) = \sum_{n_z}^{N_z} \delta(E - E_{n_x n_y n_z})$ and then broadening the energy levels by Gaussian or Lorentzian forms, i.e.,

$$g_{n_x n_y}(E) = \begin{cases} \frac{L_z}{\pi \hbar} \sqrt{\frac{m^*}{2[E - E_{n_x n_y 0}]}} \Theta(E - E_{n_x n_y 0}) & \text{Analytic,} \\ \sum_{n_z} \frac{1}{\gamma \sqrt{2\pi}} e^{-\frac{(E - E_{n_x n_y n_z})^2}{2\gamma^2}} & \text{Gaussian,} \\ \sum_{n_z} \frac{1}{\pi} \frac{\gamma}{(E - E_{n_x n_y n_z})^2 + \gamma^2} & \text{Lorentzian.} \end{cases} \quad (\text{B.6})$$

Here, we would like to point out that by varying the values of L_z and N_z , one can alter the form of both DOS and, accordingly, the conductance steps. Figs. B.1-B.3 present the different cases. In Fig. B.1, the ideal conductance steps are achieved by a dense energy spectrum, i.e., proper 1D DOS. In Figs. B.2-B.3, we ruin the conduction steps by sparsing the energy spectrum by reducing the values of L_z and/or N_z . These figures all together, indicates the evolution of ideal conduction steps from the Dirac delta function-based conduction peaks or vice versa.

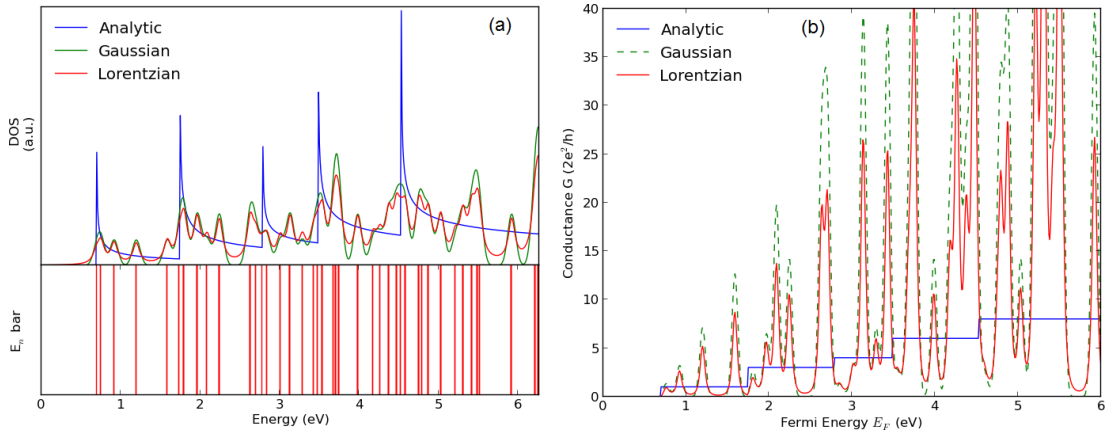


Figure B.2: Same as Fig. B.1 but $L_z = 5$ nm and $N_z = 10$ are taken to ruin the step-like conductance.

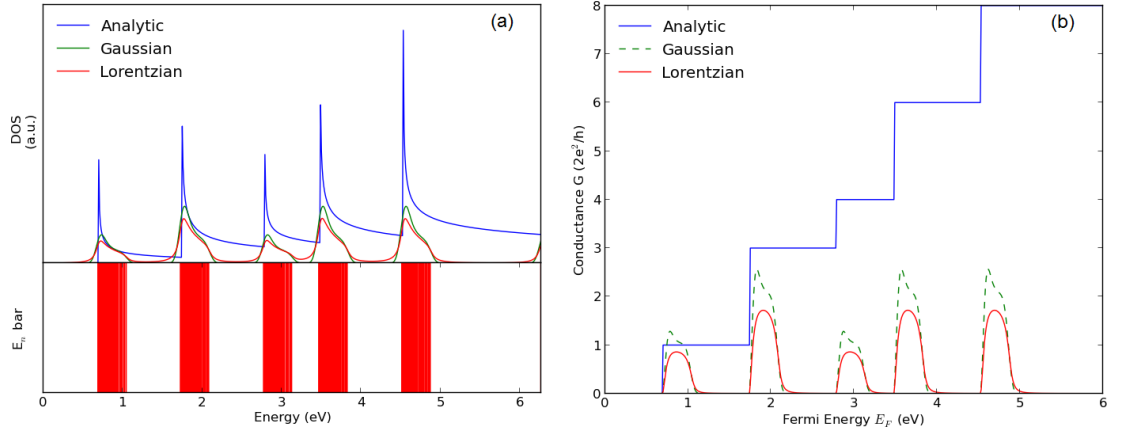


Figure B.3: Same as Fig. B.1 but $L_z = 100$ nm and $N_z = 50$ are taken to deliberately detriment the step-like conductance.