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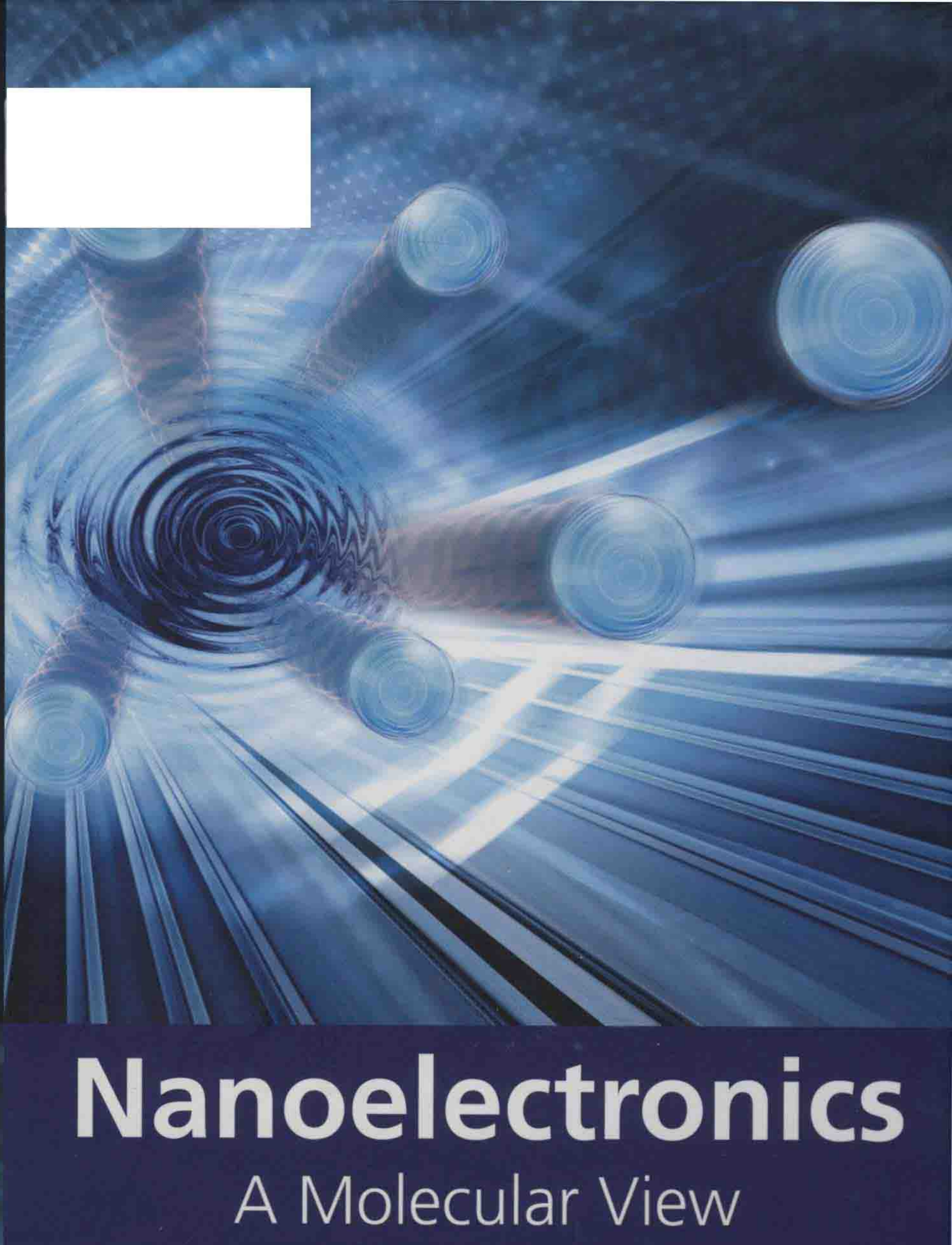

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A Molecular View

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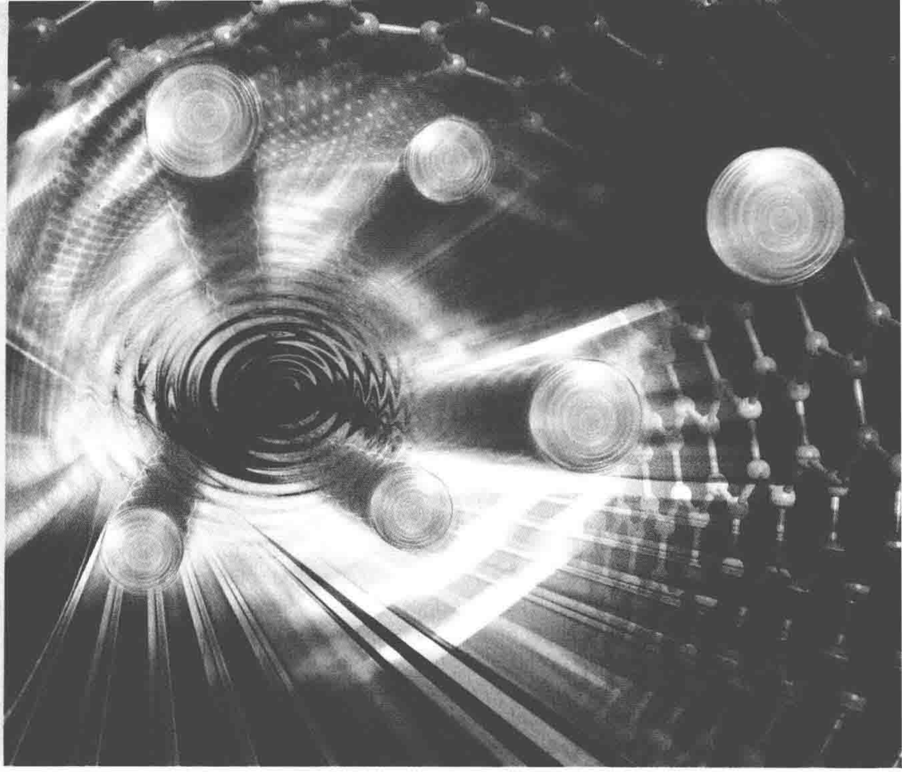

Nanoelectronics

A Molecular View

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To my parents, who taught me to dream, and to my wife and kids who help me keep it real

Preface

A popular movie back in the 60s was "Fantastic Voyage", based on a novel by Harry Kleiner, where a group of scientists were miniaturized and injected into the body of an injured scientist to fix his brain damage. The movie had a more modern update for my generation, "Inner Space", also a fun watch. Beyond the specific plot points, what drove these movies was the venue — imagining the action and adventure swirling around in a miniature unfamiliar world — a universe we carry in us every day but rarely get to observe at the level of detail that the movies deftly portrayed.

The emergent fields of nanoscience and nanotechnology draw natural comparisons to those movies. It is after all, the popular view of 'nano' among much of the public, fueled by novels like Michael Crichton's "Prey". But this book is not about injecting nanobots into the human body. The comparison I draw here is less literal, yet technologically more immediate. This book is also about a fantastic voyage — that of an electron coursing through various materials, negotiating impurities, junctions, surfaces, interfaces. With the advent of advanced spectroscopic tools, growth of emergent materials, the evolution of computational modeling, we can now 'peek under the hood' and participate in this incredible journey directly. The screenplay of this movie is also filled with twists and intrigues — the electrons sometimes behaving like classical particles jostling with each other, sometimes as waves interfering, occasionally shaking up the surrounding lattice of atoms by emitting phonons or absorbing photons, rushing to deplete their charges under the action of a gate, repelling each other through Coulomb interactions, correlating charges, locking spins. It is indeed an action-filled script with a busy cast of characters.

Beyond the intellectual exercise of visualizing and deconstructing electron dynamics, what fascinates is that the emergent fields of nanoscience and technology rely greatly on such a molecular understanding of current flow — in chemical reactions, surface processes, metal insulator transitions or ultrasmall switches. Today's semiconductor chips are getting unmanageably hot from the sheer volume of billions of transistors operating together in our smartphones and tablet computers. As a result, they undergo continuous make-overs, in architecture, material embodiment and even physical principles. Not only logic, but memory, sensing and pattern recognition, solid state lighting, thermoelectrics and solar cells are all seeing their own scaling rules lead them naturally towards exploration and redesign driven by their fundamental molecular structures. A thorough understanding of device conduction down to its molecular detail is often essential to understanding, to its continued miniaturization and sustained performance.

I teach two complementary engineering classes fairly regularly. One is a top-down introduction to solid-state electronic devices based on classical Newtonian physics. A large number of traditional devices such as bipolar junction transistors (BJT) and conventional metal oxide semiconductor field effect transistors (MOSFETs), Schottky diodes, high electron mobility transistors (HEMTs), solar cells and photodetectors can be understood in terms of drift-diffusion equations, often reduced to simple circuit diagrams. The other course I teach, for grads/undergrads, is a bottom-up introduction to nanoelectronics. That course introduces quantum transport physics, and is suitable for emerging materials and devices such as tunnel junctions, graphene, spintronics, silicon nanowires and quantum dots.

Three lessons emerged from these courses, plus my own research over the years as a physicist in an engineering department dabbling with quantum chemistry and materials science.

(1) A proper methodology must be introduced that merges the top down and bottom up viewpoints, connecting established CAD tools with more esoteric transport formalisms used by physicists. This is essential since even conventional devices such as commercial MOSFETs have a large fraction of electrons (currently $\sim 70\%$) acting ballistically, requiring us to study processes beyond top down scattering and diffusion.
(2) These connections are better achieved through hands-on examples and toy models that connect chemistry with bandstructure and many-body

physics. Such a combined viewpoint is not within the purview of isolated physics, chemistry, and engineering courses, and is truly interdisciplinary.
(3) At the same time, students must be able to model real materials hands-on and make quantitative and predictive statements.

This book arose from that realization, and aims for a few specific goals.

1. Combining a bottom-up approach to electronics with classical top-down viewpoints popular in device simulation tools. In fact, going a step further by outlining a mosaic of transport theories by drawing hierarchies and interrelationships connecting them — not only between classical and quantum, but also between collective and single particle behavior.

2. Introduce a comprehensive molecular view that can be used to understand not just molecular electronics, but transport through other 'molecules' such as graphene ribbons, magnetic junctions and quantum dots. A viewpoint that can nonetheless scale up to conventional bulk solids.

3. Emphasize the unique physics that emerges as we shrink down our devices — the orbital symmetries, basis sets, quantum effects like exchange (which device theorists typically include in a limited embodiment of Pauli exclusion) start to become dominant rather than dormant.

4. A unified treatment of scattering ranging from elastic impurity to inelastic and incoherent scattering, going between 'quick and dirty' phenomenological treatments to more rigorous 'molecular' effects such as inelastic tunneling spectroscopy or polaron formation.

5. Handling correlation effects in transport, where electrons find clever ways to lock their dynamics and lower their energy costs. Correlation effects are already relevant for today's technology (semiconductor nanocrystal memory relies on Coulomb blockade), but could be even more relevant in future with Mott switches and other correlation-based devices.

6. Provide a lot of 'hands-on' examples (I refer to those as *case studies*) to illustrate the principles by doing, rather than saying. I believe a few good examples save me several pages of uninspired formalism. In the spirit of the 'molecular view', I frequently illustrate my points with prototypical molecules. I use the hydrogen (H_2) molecule to illustrate bonding,

exact diagonalization, configuration interaction and the Gutzwiller approach, and benzene to illustrate bandstructure, resonance, hybridization, Coulomb blockade, gateability and a scale-up to graphene. And I try to provide words and pictures behind the operational equations, so that they make not just mathematical, but intuitive sense.

7. Connecting these studies with fundamentals of low-power computing, bypassing the Boltzmann limit and exploring some prototypical, unconventional switching devices. Through these examples, I seek to bring physical concepts to the engineers, and bring engineering concepts to the physicists.

This book comes at the heels of a remarkable set of volumes. Volume 1, "Lessons from nanoelectronics — A New Perspective on Transport" by Supriyo Datta provides a wonderful introduction to quantum transport of charges, spins and heat. Volume 2, "Near-equilibrium Transport: Fundamentals and Applications" by Mark Lundstrom focuses on low-bias transport. This volume extends these techniques to bring into its fold chemistry, molecular solids and emerging low-power devices. We start with the motivation — both the intellectual pursuit driving physicists (Chapter 1) and the practical device angle relevant for engineers (Chapter 2). Next, we describe the commonly used quantum mechanical tools in Chapters 3-6, the underlying language for these descriptions. I recap quantum physics, quantum chemistry and band theory in Chapters 3-5. In Chapter 6, I introduce second quantization needed to understand correlation effects. In Chapter 7, I introduce the concept of Green's functions, which lie at the heart of the 'bottom-up' transport theory used all over the book.

It is fair to say that most functional electronic devices, chemical and biological processes involve venturing far from equilibrium, requiring a thorough understanding of transport theory. Chapter 8 gives a bird's eye view of the transport mosaic, from classical to quantum. Chapter 9 starts with classical drift diffusion, connecting it rigorously with our intuitive picture of an overdamped Newtonian particle kicked around by thermal white noise. Chapter 10 discusses semiclassical transport, while Chapter 11 takes us to the Nonequilibrium Green's Function (NEGF) relevant for quantum transport. We follow Datta's derivation of the main NEGF equations from simple one-electron quantum mechanics with open, thermalized boundary conditions. We also describe the more mainstream, Keldysh contour theoretical formulation of NEGF. For weak interactions, the two approaches converge.

For stronger interactions, the Keldysh approach allows us to extend established perturbative techniques from equilibrium many body physics such as Feynman diagrams, albeit on a Keldysh contour. For very strong interactions, we may need to improvise non-perturbative approaches that I discuss in Chapter 27.

Chapters 12-13 deal with simple limits of the NEGF equations. For coherent, ballistic flow, the equations reduce to the Landauer formula for a two-terminal device (and Landauer-Büttiker for multi-terminal). For the opposite end of scattering dominated devices, we recover Ohm's Law. The beauty of NEGF is that it allows us to incorporate partial scattering, so we can interpolate between the two limits, and independently study the role of momentum, phase, spin and energy scattering.

The most voluminous part of this book is on the adventures of the electron in its journey. In contrast to other books or monographs on quantum transport, the classification I choose to pursue is 'behavioral'. My aim here is to start with the flow mechanisms that are simplest to understand and model, and then add complexity in incremental layers from one chapter on to another. Accordingly, I start with quantum tunneling in Chapter 14. Beyond a standard WKB approach, I show how to convert a transmission into an actual current across a thin film and how to extend it to small molecular layers. Chapter 15 extends this to tunneling with an additional symmetry index. I discuss how angular symmetry arising from the orbital chemistry of the tunneling electrons can and already has made an impact in oxide technology, how spin selection rules further control the tunneling probability in tunnel magnetoresistance devices, and finally how the behavior of pseudospins controls Klein tunneling and Berry phase in graphene and topological insulator pn junctions.

From tunneling, we move to regular two-terminal conduction across lower dimensional systems, with emphasis on graphene in Chapter 16 and molecular conduction in Chapter 17. Since these systems are small enough to be near ballistic (i.e., electron does not scatter until it reaches the contacts), the machinery of quantum transport becomes indispensable in explaining their measured transport characteristics even qualitatively.

We spend some time talking of gating and switching in Chapter 18, connecting to the device world and its needs. Beyond conventional electrostatic switching, we talk of unconventional switches such as conformational relays in Chapter 19 (more generally, configurational gating), two terminal switches and resistive memory elements in Chapter 20, connecting to neuromorphic systems and stochastic processes such as random telegraph noise. In Chapter 21, we look at the behavior of weakly interacting electrons in presence of a magnetic field, creating skipping orbits and Landau levels, Hofstader butterflies in a lattice, and quantum Hall plateaus. We discuss how one can use noncollinear magnetization between two magnets to generate a torque in order to write information for scalable non-volatile storage.

Researchers working on NEGF often limit themselves to the simplified Landauer equation valid for non-interacting or weakly interacting systems. A significant difference between Landauer and NEGF manifests itself in presence of scattering (Chapters 22-24) and of many-particle interactions (Chapters 25-27). There are phenomenological ways to introduce scattering such as mean free paths and Büttiker probes — and more rigorous descriptions based on the Keldysh formalism that capture much more intricate microscopic details. A cornucopia of phenomena arise from scattering, from thermalization and current saturation to self-heating and phonon bottlenecks, polaronic shifts and vibrational sidebands. My aim in Chapters 22-24 is to connect and illustrate these approaches — the rigorous and the not-so-rigorous. The Caroli/Meir-Wingreen formula serves as a glue between the Landauer-NEGF approaches. One may wonder why a mainstream device physicist needs to venture beyond Landauer theory to do NEGF, especially as devices head towards ballisticity. However, every serious device theorist should at the least include screened Coulomb interactions in Poisson's equation, and some dephasing to kill spurious quantum interference effects (on occasion we also need inelastic phonon scattering) — whereupon an explicit treatment of the nonequilibrium Green's function G^n becomes mandatory.

Correlated systems provide the ultimate challenge in electronic structure theory. The challenge is significantly compounded for nonequilibrium properties like current, which in general turns out to be much harder to calculate in the face of myriads of excitations out of the ground state. One needs to respect the symmetry/antisymmetry properties of the entire multielectron wavefunction while dealing with its two particle Coulomb interactions. Chapter 25 introduces the many body (Fock) space and Chapter 26 introduces the multielectron transport formalism and the challenges it brings, especially with regard to the proper treatment of coherent broadening of one electron transitions in a many-electron manifold. Chapter 27 introduces some of these broadening effects non-perturbatively through the equation of motion technique. We generalize it to solids to study the Mott transition. Importantly, we argue that we can in principle use conventional NEGF to calculate a correlation current, by including the corresponding non-perturbative self-energy matrix into the Meir-Wingreen formula.

Finally in Chapters 28-30, we bring together our equations and overall understanding to explore examples that are relevant to the fundamental physics of low power, subthermal switching. We speculate on how to beat the Boltzmann tyranny to switch a channel efficiently. Only time will tell if any of them end up being practical. However, they are good test cases to apply our equations and explore the interesting physics that allows them, in principle, to beat the aforementioned limit. More excitingly, as we will argue, almost every example in this category requires the full advanced machinery of quantum and/or correlated transport, well beyond conventional drift-diffusion equation.

A project like this involves many I am indebted to. My family — a constant source of inspiration over the years. My teachers in school and college, humble and yet immensely inspiring, who got me started on the road to scientific exploration. My mentors spanning my research career, each with definitive contributions to quantum transport — John Wilkins, Supriyo Datta and Mark Lundstrom — who taught me to think big and think simple. My scientific collaborators over the years, too many to name individually. Various funding agencies and program managers, from NSF to DoD to SRC that provide the much needed and well appreciated financial resources to pursue the research necessary for the studies. My students and postdocs, often the ones silently carrying out much of the actual gruntwork underlying these studies. A special shout out to Carlos Polanco, and his unflagging commitment to reading and rereading, editing and opining at every stage of this project while balancing his thesis on interfacial thermal conductance. A strong thank you to Jianhua Ma for helping secure permissions and final edits. To the publisher, thank you for providing such an exciting venue to collect my thoughts and cumulative wisdom.

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