

# High-Fidelity Modeling of Single-Molecule Quantum Electronic Devices

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## ABSTRACT

We examine device physics and study characteristics of single-molecule multi-terminal electronic devices. These devices exhibit quantum phenomena such as highly nonlinear tunneling, resonance and other. The device physics is based on the controlled propagation of electrons. The aforementioned *microscopic* devices must be examined quantum-mechanically. By applying quantum mechanics and advanced numeric schemes, we perform the device-level analysis researching propagation, transitions and interactions of electrons. Our ultimate objective is to analyze the controlled electron transport, study tunneling, evaluate performance and assess device capabilities. Using three-dimensional Schrödinger and Poisson equations, we examine the electron transport by numerically solving the above mentioned equations using a self-consistent scheme. The controlled electron transport, super-fast transitions and highly nonlinear tunneling are observed. Solutions are applicable to various sensing and processing devices.

**Keywords:** electron, modeling, molecule, quantum mechanics, tunneling

## 1. INTRODUCTION

For *macroscopic* semiconductor device one examines the device physics by applying the basic laws. The steady-state and dynamic characteristics are straightforwardly obtained. For various solid-state electronic devices, such as FETs, BJTs and other, this analysis is well-established, and, the deviations are straightforward as reported in [1].

Recently, *microscopic* sensing, interfacing and processing devices were introduced. These devices operate utilizing quantum phenomena. The *microscopic* molecular devices are fundamentally distinct as compared with nanoscaled *macroscopic* solid-state devices.

High-performance lasers, quantum-well resonant tunneling diodes and FETs, Schottky-gated resonant tunneling, heterojunction bipolar, resonant tunneling bipolar and other transistors were introduced, demonstrated, tested and deployed. These solid-state devices significantly enhanced the classes of microelectronic devices. The

forementioned devices utilize quantum phenomena and effects. However, these devices are *macroscopic* because they operate utilizing the immense number of electrons, obey classical statistics and electrostatics, fabricated using conventional microelectronic technologies, etc.

Departing from planar solid-state microelectronic devices, molecular devices were extensively studied [2-5]. Various single-molecule two-terminal devices were synthesized and experimentally characterized [2-5]. The experiments demonstrate some inconsistencies which may be analyzed by examining quantum phenomena and effects. There is a need to further analyze multi-terminal three-dimensional-topology molecular devices. These devices are envisioned to be used in emerging three-dimensional neuronal hypercells (<sup>n</sup>hypercell) which establish sensing, interfacing and processing *fabricis*. Molecular devices can be formed (synthesized) using cyclic molecules, compounds, cages and other aggregates with a carbon interconnecting framework forming processing <sup>n</sup>hypercells [5]. With a focus on practical quantum-effect devices, we concentrate on devices for which the Heisenberg uncertainty principle can be guaranteed leading to testing, characterization and evaluation. The aforementioned features are essential to design practical systems.

## 2. CYCLIC SINGLE-MOLECULE MULTI-TERMINAL ELECTRONIC DEVICES AND *FABRICIS*

Figures 1 report single-molecule electronic devices with overlapping atomic orbitals. These devices may have the *input*, *control* and *output ports*. The orbitals of the terminal atoms can be hybridized to the adjacent atoms by electron-pair covalent bonds forming device-to-device interconnect. These molecules are covalently bonded *directly* or using linkers and spacers. This may allow one to establish sensing or processing *fabricis*. Correspondingly, the injected electron propagate, and, the controlled propagation of the electron must be accomplished.

Using three-, six- and multi-terminal devices, one may attempt to visualize classical logic gates as illustrated in Figure 2. Though the aforementioned binary gates are widely realized using ICs, molecular processing *fabricis* will empower quantum-mechanical processing schemes,

solutions, interfacing and networking. The device physics of *microscopic* devices is fundamentally distinct as compared to semiconductor devices. One may be unable to apply the voltage to the *control ports*. Control of molecular devices is examined in the following sections.

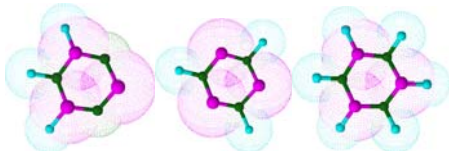


Figure 1. Three- and six-terminal cyclic molecule with a carbon interconnecting framework

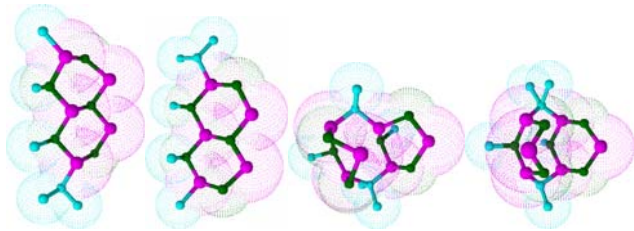


Figure 2. Naive representation of AND, NAND, OR and NOR gates

The cyclic molecules can be used to form two-, three- and  $n$ -terminal devices. The proposed solution:

- Ensures a practical *bottom-up* synthesis at the device and system levels;
- Guarantees aggregability, repeatability and robustness to form complex sensing, interfacing and processing *fabrics*;
- Results in the experimentally characterizable devices and systems.

### 3. CONTROL OF MOLECULAR ELECTRONIC DEVICES

It is imperative to examine the functionality, characteristics, electron transport and other quantum-mechanical quantities in the molecules and molecular complexes. Consider the motion and propagation of *delocalized* electrons in single-molecule devices. The propagation of electrons should be controlled to achieve device functionality. The propagation and *states* of electrons can be controlled by using external excitations

$$\mathcal{E}(t, \mathbf{r}) = [V_{\mathcal{E}}(t, \mathbf{r}), \mathbf{E}_{\mathcal{E}}(t, \mathbf{r}), \mathbf{B}_{\mathcal{E}}(t, \mathbf{r})].$$

This  $\mathcal{E}(t, \mathbf{r})$  changes the time- and spatial-varying potential function  $\Pi(t, \mathbf{r})$ , volume charge density  $\rho(t, \mathbf{r})$ , electric field intensity  $\mathbf{E}(t, \mathbf{r})$ , vector magnetic potential  $\mathbf{A}(t, \mathbf{r})$ , etc. Time- and spatially-varying  $\mathcal{E}(t, \mathbf{r})$  could be potential  $V_{\mathcal{E}}(t, \mathbf{r})$  or electromagnetic fields  $\mathbf{E}_{\mathcal{E}}(t, \mathbf{r})$  and  $\mathbf{B}_{\mathcal{E}}(t, \mathbf{r})$ .

One may use the side groups ensuring the variations of the potential surfaces  $\Pi(t, \mathbf{r})$ , e.g., engineering the time- and spatially-varying energy barriers. The aforementioned features guarantee:

1. Controlled quantum *state* transitions and evolutions due quantum phenomena exhibited;
2. Controllable electron propagation, transport, tunneling, scattering, hopping, etc.;
3. Quantum interactions such as highly nonlinear engineered tunneling, resonance, etc.

These features lead to the overall functionality and operability. The device physics of these devices is based on:

- Quantum phenomena (quantum effects, interactions, etc.);
- Controlled potential- and field-assisted electron transport.

For example, as one considers the evolution and propagation of electrons in the time- and spatial-varying potential  $\Pi(t, \mathbf{r})$ , the changes of  $\Pi(t, \mathbf{r})$  and Hamiltonian result in varying tunneling  $T(E)$ , probabilities, quantum interactions, etc. One considers the propagation of electrons between the *input* and *output ports* under time- and spatially-varying  $\mathcal{E}(t, \mathbf{r})$ . The device is controlled by varying  $\mathcal{E}(t, \mathbf{r})$  guaranteeing the controlled propagation of electrons. For example,  $T(E)$  varies. To some extent,  $T(E)$  may be analogous to the well-known  $I$ - $V$ ,  $G$ - $V$  and other characteristics of semiconductor devices. However, for *microscopic* devices, the  $I$ - $V$  or  $G$ - $V$  characteristics may be obscure. Therefore, quantum-mechanical quantities, such as  $T(E)$  and probabilities, are applied. The single-molecule *microscopic* devices under consideration guarantee:

- Fundamentally consistent device physics;
- Device testability, characterization and evaluation because the Heisenberg uncertainty principle  $\sigma_E \sigma_T \geq \frac{1}{2} \hbar$  is met;
- Synthesis, aggregation and interfacing capabilities forming  $\aleph$ hypercells and *fabrics*.

### 4. MODELING AND ANALYSIS OF A SINGLE-MOLECULE MICROSCOPIC DEVICE

For heterojunction microelectronic devices, one usually solves one-dimensional Schrödinger and Poisson equations applying statistical thermodynamics (Fermi-Dirac distribution function) and electrostatics [1, 5]. For the studied *microscopic* devices, conventional approaches cannot be applied. The distribution functions and statistical mechanics postulates may not be applied.

We perform quantum-mechanical modeling for the studied molecular devices which are reported in Figure 1. To ensure data-intensive analysis, heterogeneous simulations are performed. For a single-molecule electronic

device, consider 9 atoms with motionless protons with charges  $q_i$ . The radial Coulomb potentials are

$$\Pi_i(r) = -\frac{Z_{eff} q_i^2}{4\pi\epsilon_0 r}$$

For example, for carbon  $Z_{effC}=3.14$ .

A three-dimensional problem cannot be simplified. Using the spherical coordinate system, we solve the Schrödinger equation

$$-\frac{\hbar^2}{2m} \left[ \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial \Psi}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial \Psi}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2 \Psi}{\partial \phi^2} \right] + \Pi(r, \theta, \phi) \Psi(r, \theta, \phi) = E \Psi(r, \theta, \phi).$$

For the stand-alone first and second cyclic molecules, reported in Figure 1, the *input*, *control* and *output ports* are formed by covalent bonds between C-P and C-N atoms. For *microscopic* systems under our consideration, it is virtually impractical to find the analytic solution. The wave function  $\Psi(t, \mathbf{r})$  is numerically derived from the wave functions of valence electrons  $\Psi_{j(nlm)}(t, \mathbf{r}_j)$ . We represent the wave functions by using the separation of variables concept. That is

$$\Psi_j(r, \theta, \phi) = R_j(r) Y_j(\theta, \phi).$$

The radial and angular equations are solved. By applying the Hartree-Fock concept, the Schrödinger and Poisson equations are discretized and numerically solved [5]. The magnitude of the time- and spatially-varying potential is bounded due to the thermal stability and energetics of the molecule, e.g.,

$$|\mathbf{E}_\varepsilon(t, \mathbf{r})| \leq \mathbf{E}_{\varepsilon \max}(t, \mathbf{r}),$$

The Schrödinger and Poisson equations are solved using a self-consistent algorithm [5]. Our goal is to examine the device physics and derive the baseline performance characteristics.

For different  $\mathbf{E}_\varepsilon(t, \mathbf{r})$  and perturbations, the resulting transmission characteristic  $T(E)$  for the injected electron are found using  $\Psi_j(t, \mathbf{r}_j)$ . Though the valence electrons, characterized by quantum numbers  $(n, l, m_l)$ , may assume different  $\mathbf{r}_j$  and  $E_{nj}$ , it is found that the processable characteristics can be achieved. However,  $T(E)$  can be significantly affected by perturbations and disturbances due to interference, noise, etc. Self-consistently solving the Schrödinger and Poisson equations, we consider the valence orbitals for *delocalized* electrons. The resulting  $T(E)$  for unperturbed and perturbed cases are documented in Figures 3,  $E_{\varepsilon \max}(r) = 1 \times 10^8$  V/m. The transmission characteristics  $T(E)$ , which depend on an injected electron energy, are reported. As perturbations increase,  $T(E)$  characteristics slightly change.

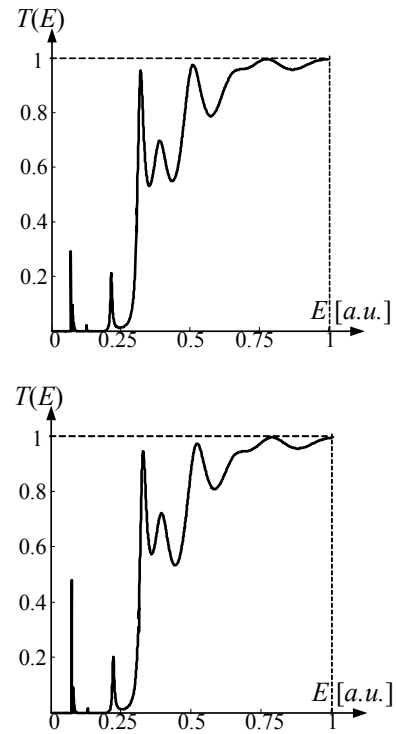


Figure 3. Transmission characteristics  $T(E)$  for an injected electron: (a) Unperturbed cyclic molecule; (b) Molecule under external electric field perturbations

The probability of the leaving electrons at the *output port*  $p_{\Delta V}$  is characterized by  $T(E)$ . Using the wave function, the probability of electron in  $\Delta V$  is

$$p_{\Delta V} = \int_V \Psi_{j(nlm)}^*(t, \mathbf{r}_j) \Psi_{j(nlm)}(t, \mathbf{r}_j) dV.$$

This yields the following expression

$$p_{\Delta V} \cong T(E).$$

The traversal time of electron transport is derived from

$$\tau(E) = \int_{r_0}^{r_f} \sqrt{\frac{m}{2[\Pi(\mathbf{r}) - E]}} d\mathbf{r}.$$

It is found that  $\tau$  varies from  $1.75 \times 10^{-15}$  to  $2.31 \times 10^{-15}$  sec. Hence, the proposed device ensures super-fast switching.

For quantum-effect *microscopic* devices, one may not use the  $I-V$  or  $G-V$  characteristics, electron mobility  $\mu_n$  and other descriptive features of *nanoscaled* semiconductor devices. For example, for solid-state devices, for an immense number of electrons, using the electron velocity

$$\mathbf{v} = -\mu_n \mathbf{E}_E$$

one derives the drift current density as [1]

$$\mathbf{j} = Q\mathbf{v}.$$

For *microscopic* devices, a single photon or electron in the state  $(n, l, m_l, m_s)$  should be examined, for which, the allowed quantized energy is  $E_n$ . Departing from the Fermi-Dirac distribution statistics, one uses the quantum-mechanical statistics governed by the wave function  $\Psi_{j(nlm)}(t, \mathbf{r}_j)$ . By using  $p_{\Delta v}$  and  $T(E)$ , one may examine functionality, capabilities, baseline performance and other features. One may define a *pseudo* current (the rate of change of charge,

$$i=dq/dt)$$

or *pseudo*  $I$ - $V$  characteristics from  $T(E)$ .

However, these *naive macroscopic*-centric characteristics, quantities and results may have a limited practicality, suitability and applicability. In contrast, the derived highly-nonlinear  $T(E)$  characteristic for a single injected electron may imply and suggest multiple-state and multiple-valued processing, highly-selective sensing, etc.

One must be advised and cautioned that *aggregation* (covalent bonds with other atoms within a hypercell, *lattice* or *fabric*) may significantly refine the overall device characteristics, functionality and capabilities. Furthermore, as electron characterized by  $(n, l, m_l, m_s)$ , the quantum-mechanical statistics must be applied for the overall *microscopic* system. The measurements, characterization and evaluation may remain the impediment obstacles for *engineered microscopic* systems. The reported results also illustrate that one must ensure consistent *quantum-classical* or *classical-quantum* interconnecting schemes.

## 5. CONCLUSIONS

We reported very promising results on devising and analysis of quantum-effect *microscopic* devices. The device physics of these single-molecule sensing and processing primitives was discussed proving the overall feasibility. The fundamental, analytical and numerical results, including high-fidelity modeling and data-intensive analysis, were reported in details.

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