



# Introducing Multi-Space DFT for Nonequilibrium Quantum Transport Calculations

**Yong-Hoon Kim**  
 School of Electrical Engineering  
 Korea Advanced Institute of Science & Technology (KAIST)  
 y.h.kim@kaist.ac.kr

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## KAIST EE Yong-Hoon Kim Group

**Group Members**  
<http://nanocore.kaist.ac.kr/yhklab>

**Research staff**

- Dr. Junho Park
- Dr. Junho Lee
- Dr. Kapitan S. Rajput
- Ms. Hyo Jin Jeon

**PhD Students**

- Tae Hyung Kim
- Hyunwoo Yeo
- Ryongyu Lee
- Youmin Song

**Alumni**

- Dr. Juho Lee
- Dr. Han Seul Kim

**MS Students**

- Seunghyun Yu
- Jaewon Kim



**Funding**





## Beyond DFT: Eqm. → Non-Eqm.

**Density Functional Theory (DFT)**

- VASP
- SIESTA
- etc. etic.

**GW+BSE & time-dependent DFT**

**Non-Equilibrium Green's function (NEGF)**

**QuantumATK**

- TranSIESTA
- QuantumATK
- etc.

**Energy, structure, ...**

**@ Equilibrium**

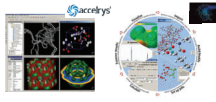

**Optical excitation, ...**

**@ Non-equilibrium**

**Quantum transport, ...**

**@ Non-equilibrium**

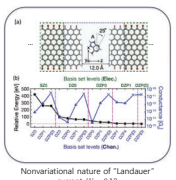
**SYNOPSIS**

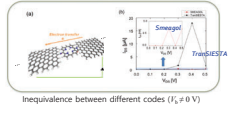
## Difficulties with NEGF (beyond-DFT methods in general)

**⊕ NEGF difficulties: Examples**

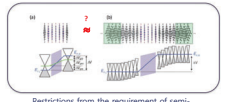
**Nonvariational nature of "Landauer" current ( $I_L \neq I_V$ )**



**Inequivalence between different codes ( $I_L \neq I_V$ )**



**Restrictions on the requirement of semi-infinite electrodes ( $I_L \neq I_V$ )**



## Origins of difficulties: Open B.C.

**DFT (Equilibrium)**

**Closed or Periodic B.C.**

$$H\psi_i = \epsilon_i\psi_i$$

$$f_{DFT}(E) = f_{FD}(E - \mu)$$

**⊕ High-reliability of simulations!!**

$$E[\chi] = \frac{\langle \chi | H | \chi \rangle}{\langle \chi | \chi \rangle} \rightarrow E[\chi] \geq E_{GS} = \langle \psi_{GS} | H | \psi_{GS} \rangle$$

- Total energy ← Variational principle

**NEGF (Non-equilibrium)**

**Open B.C.**

$$G^R = (E - H - \Sigma_L - \Sigma_R)^{-1}$$

$$G^A(E) = f_{LD}(E) + f_{RD}(E)$$

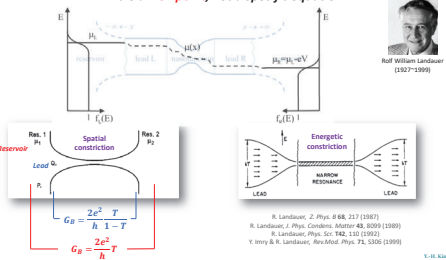
**⊕ Ambiguities??**

$$I(V) \approx \frac{e}{h} \int dE \text{Tr}(\Gamma_L G^R G^A \Gamma_R) [f_L - f_R]$$

- Current: Non-variational quantity

## cf. DFT-NEGF = Landauer + NEGF (Landauer ≠ NEGF!)

**"... it is a viewpoint, not a specific equation."**

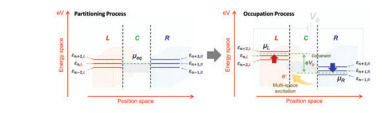


Prof. William Landauer (1927-2009)

## Alternative to Landauer picture & DFT-NEGF?

### Multi-space constrained-search DFT (MS-DFT)

**1. Steady-state quantum transport = Time-independent multi-space optical excitation** cf. Landauer viewpoint

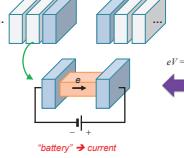


**2. Micro-canonical → Variational (constrained-search) DFT quantum transport calculation** cf. DFT-NEGF

**Quantum transport = Multi-space (space-discriminating) excitation → Variational DFT calculation of steady-state current**

Step 1. Viewpoint: Grand-canonical ("Landauer") ⇔ Micro-canonical

Di Ventura & Todorov, J. Phys. Cond. Matt. 16, 8025 (2004)



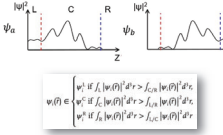
**"battery" → current**      **"capacitor" → current**

## Multi-Space constrained-search DFT: Formulation

**Quantum transport = Multi-space (space-discriminating) excitation → Variational DFT calculation of steady-state current**

Step 2. Assign  $\Psi$  to L, C, & R regions

**"locality" or "near-sightedness" in C (semi-conductors)** (W. Kohno)



$V = 0: \rho_C(\vec{r}) = \rho_C^L(\vec{r}) + \rho_C^R(\vec{r}) + \rho_C^E(\vec{r})$

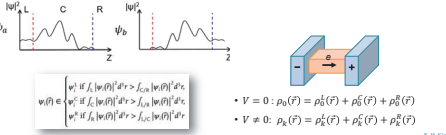
$V = \neq 0: \rho_C(\vec{r}) = \rho_C^L(\vec{r}) + \rho_C^R(\vec{r}) + \rho_C^E(\vec{r})$

## MS-DFT: Formulation – Step 2

**Quantum transport = Multi-space (space-discriminating) excitation → Variational DFT calculation of steady-state current**

Step 2. Assign  $\Psi$  to L, C, & R regions

**"locality" or "near-sightedness" in C (semi-conductors)** (W. Kohno)



## MS-DFT: Formulation – Step 3

**Quantum transport = Multi-space (space-discriminating) excitation → Variational DFT calculation of steady-state current**

Step 3. quantum transport ⇔ Multi-electrode (drain → source) excitation

cf. Variational time-independent excited-state DFT

- M. Levy & A. Nagy, Phys. Rev. Lett. 83, 4361 (1999).
- A. Görling, Phys. Rev. A 59, 3359 (1999).

For the "excited" state;

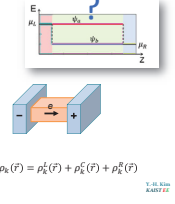
$$E_k = \min_{\psi} \int d\vec{r} \psi(\vec{r}) \rho(\vec{r}) d^2\vec{r} + F[\rho_k, \rho_L, \rho_R]$$

$$= \int d\vec{r} \psi(\vec{r}) \rho(\vec{r}) d^2\vec{r} + F[\rho_k, \rho_L, \rho_R]$$

with

$$F[\rho_k, \rho_L, \rho_R] = \min_{\psi} \int d\vec{r} \psi(\vec{r}) \rho(\vec{r}) d^2\vec{r} + V_{ext}[\psi, \rho_k, \rho_L, \rho_R]$$

→ **Constrained Search** (constraint:  $eV = \mu_R - \mu_L$ )

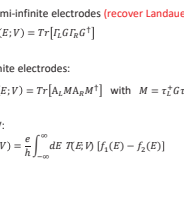


## MS-DFT: Formulation – Step 4

**Quantum transport = Multi-space (space-discriminating) excitation → Variational DFT calculation of steady-state current**

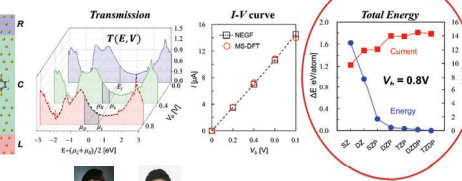
Step 4. Transmission & current as post-processing processes

- Semi-infinite electrodes (recover Landauer):  $T(E, V) = \text{Tr}[\Gamma_L G^R G^A \Gamma_R]$
- Finite electrodes:  $T(E, V) = \text{Tr}[A_M M_A M^T]$  with  $M = \tau_z^T G^R$
- I-V:  $I(V) = \frac{e}{h} \int dE \text{Tr}[\Gamma_L (f_L - f_R) \Gamma_R]$



## MS-DFT advantages 1. "Non-equilibrium" total energy

MS-DFT (microcanonical) vs NEGF (grand-canonical) → Key implication:



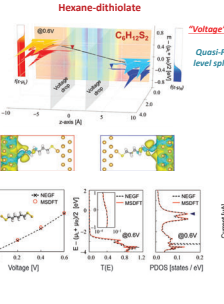
**Total Energy**

$V_b = 0.8V$

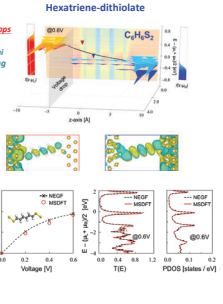
Dr. Han Seul Kim, Dr. Juho Lee

## 2. Quasi-Fermi levels (Electrochemical potential drops)

**Hexane-dithiolate**

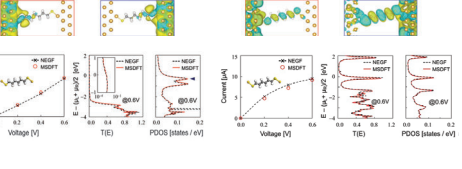


**Hexatriene-dithiolate**



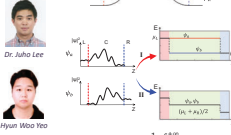
**"Voltage" drops**

**Quasi-Fermi level splitting**



## Explicit (implicit) QFLs within MS-DFT (DFT-NEGF)

Occupation rule? → Important to maintain the **separate (non-local) QFLs!**



Dr. Junho Lee

Hyunwoo Yeo

J. Lee, H. Yeo, & Y.H.K., PNAS 117, 10514 (2020)

cf.  $n(\vec{r}) = \frac{1}{2\pi} \int dE G^R(\vec{r}, \vec{r}; E)$

$= \frac{1}{2\pi} \int dE \text{Tr}[(A + f_L A_L) G^R \Gamma_R G^A]$

$\psi_i \in \begin{cases} \psi_i^L & \text{if } \int d\vec{r} |\psi_i(\vec{r})|^2 > \int d\vec{r} |\psi_i^L(\vec{r})|^2 \\ \psi_i^R & \text{if } \int d\vec{r} |\psi_i(\vec{r})|^2 > \int d\vec{r} |\psi_i^R(\vec{r})|^2 \\ \psi_i^E & \text{if } \int d\vec{r} |\psi_i(\vec{r})|^2 > \int d\vec{r} |\psi_i^E(\vec{r})|^2 \end{cases}$

## 3. 2D vdW devices: e.g. Gr/hBN/Gr heterojunctions

**Experiment**

- FET switching with On/Off  $\approx 1 \times 10^4$
- Negative Differential Resistance (NDR)

L. Britnell et al. Science 335, 942 (2012)

L. Britnell et al. Nat. Commun. 4, 1794 (2013)

**Theory**

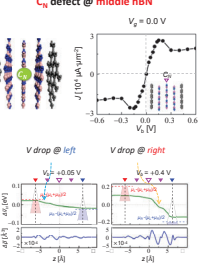
- Only semi-classical: Bardeen approach
- No ab initio: Difficulty with DFT-NEGF

Feenstra et al. J. Appl. Phys. 111, 4 (2012)

## MS-DFT → Gr/defective hBN/Gr: I-V & voltage drop

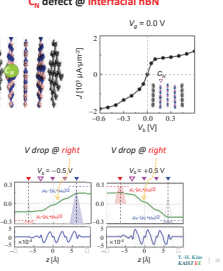
**C<sub>60</sub> defect @ middle hBN**

$V_b = 0.0V$



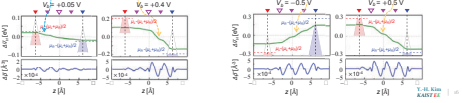
**C<sub>60</sub> defect @ interfacial hBN**

$V_b = 0.0V$



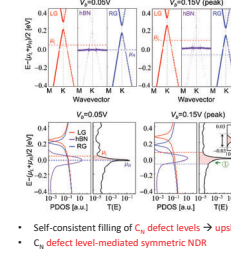
**V drop @ left**      **V drop @ right**

$V_b = 0.05V$        $V_b = 0.4V$

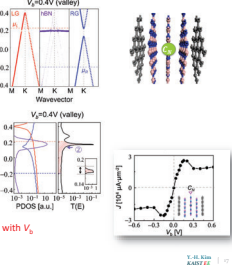


## Gr/defective hBN/Gr: C<sub>60</sub> @ middle hBN → symmetric NDR

$V_b = 0.05V$        $V_b = 0.15V$  (peak)       $V_b = 0.4V$  (valley)

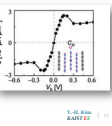


$V_b = 0.05V$        $V_b = 0.15V$  (peak)       $V_b = 0.4V$  (valley)



**Self-consistent filling of C<sub>60</sub> defect levels → upshift with  $V_b$**

**C<sub>60</sub> defect level-mediated symmetric NDR**

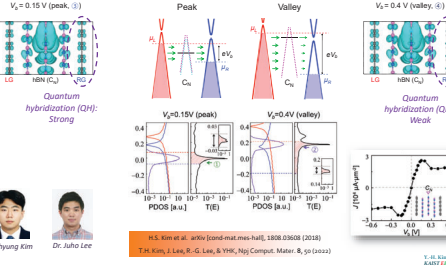


## Mechanism: Quantum Hybridization NDR

$V_b = 0.15V$  (peak, ⊕)       $V_b = 0.4V$  (valley, ⊖)

**Quantum hybridization (QH): Strong**

**Quantum hybridization (QH): Weak**



Dr. Junho Lee

H.S. Kim et al. arXiv [cond-mat.mes-hall], 1808.03608 (2018)

T.H. Kim, J. Lee, R.-G. Lee, & Y.H.K., NgJ Comput. Mater. 8, 50 (2022)