제3회 전자구조계산 겨울학교

제1원리 양자수송 계산 – 강의 3

1st-Principles Quantum Transport Calculations

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KAIST EE

강의 계획

강의 1: 배경/동기, 열린 양자계(Open quantum systems) 계산

강의 2: 비평형 양자계(Non-equilibrium quantum systems) 계산

강의 3: 양자수송의 새로운 관점 - 다공간 여기

Viewpoint: 1st-principles







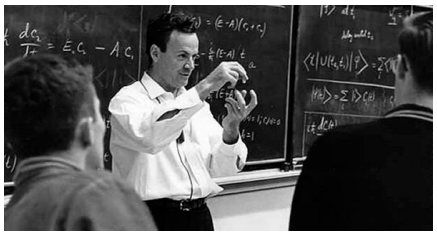
"First Principles"?

TED lecture (~ 1:20)
https://www.youtube.com/watch?v=0JQXoSmC1rs&t=10s

"어떤 아이디어를 내고 그것을 실현할 때 내게 가장 큰 도움을 준 것은 '물리학'이다. 물리학은 생각을 전개하기에 좋은 구조로 되어 있다. 어떤 것의 근본 원리와 그로부터 나온 이유만 생각하게 해준다."

물리학에서는 '유추(analogy)'가 아닌 '원리(principle)'로 사고를 전개하지만 보통사람은 일반적으로 유추를 통한 추론을 근거로 일한다. …
그런데 앞서 누구도 시도한 적 없는, 즉 완전히 새로운 일에 도전할 경우 유추는 별다른 도움이 되지 않는다. …
전례가 없는 새로운 물건을 만들어내야 할 때는 기본 원리로 돌아가 모든 대상을 재검토해야 한다.

Viewpoint: 1st-principles





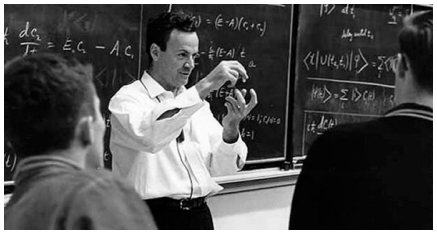
Physics 1933

Richard Feynman (1918~1988)

❑ **Q.** *"If, in some cataclysm, all of scientific knowledge were to be destroyed, and only one sentence passed on to the next generation of creatures, what statement would contain the most information in the fewest words?"*

❑ **A.** *"I believe it is the* ***atomic hypothesis*** *that all things are made of atoms — little particles that move around in perpetual motion, attracting each other when they are a little distance apart, but repelling upon being squeezed into one another. In that one sentence, you will see, there is an enormous amount of information about the world, if just a little imagination and thinking are applied."*

Focus of this lecture: "Viewpoint"





Physics 1933

Richard Feynman (1918~1988)

❑ **Feynman Lectures 2-1 "Understanding Physics"**

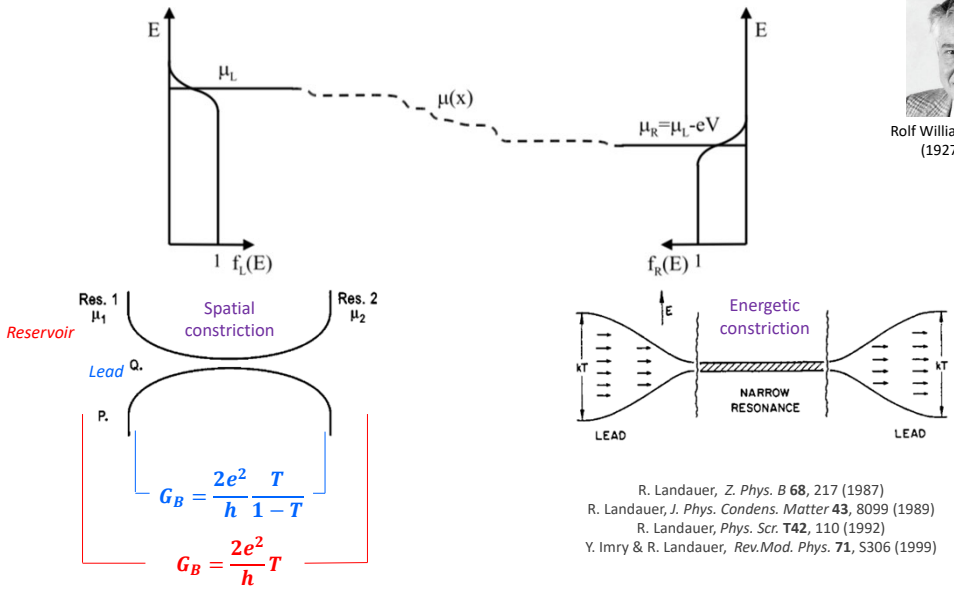
"The physicist needs a facility in looking at problems from several points of view. … There is only one precise way of presenting the laws, and that is by means of differential equations. … They say: "… there is nothing which is not contained in the equations. … if I understand them mathematically inside out, I will understand the physics inside out." Only it doesn't work that way. Mathematicians … fail because … it is necessary to have a much broader understanding of the equations. … A physical understanding is a completely unmathematical, imprecise, and inexact thing, but absolutely necessary for a physicist.

Landauer "picture" for quantum transport

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



Rolf William Landauer (1927~1999)



R. Landauer, *Z. Phys. B* **68**, 217 (1987)
R. Landauer, *J. Phys. Condens. Matter* **43**, 8099 (1989)
R. Landauer, *Phys. Scr.* **T42**, 110 (1992)
Y. Imry & R. Landauer, *Rev.Mod. Phys.* **71**, S306 (1999)

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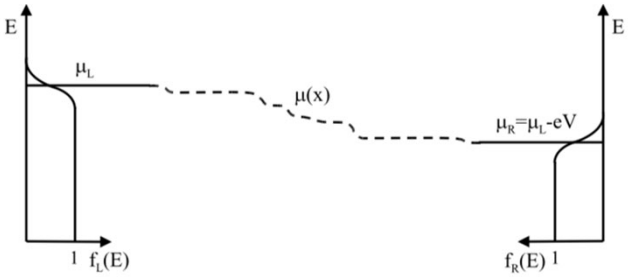




Rolf William Landauer
(1927~1999)

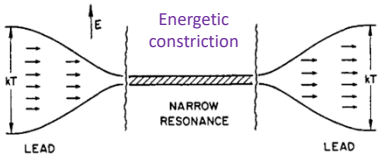
- Landauer "condition": ∃ *reservoirs*

$$\mathcal{E} = \boldsymbol{E} - \nabla\bar{\mu}/e$$

→ *Drift* → *Diffusion*

$$\Delta\mu(\boldsymbol{r},t) = e\,\Delta\phi(\boldsymbol{r},t) + \Delta\bar{\mu}(\boldsymbol{r},t)$$

Electrochemical potential | *Electrostatic potential* | *Chemical potential*



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Landauer "picture" for quantum transport

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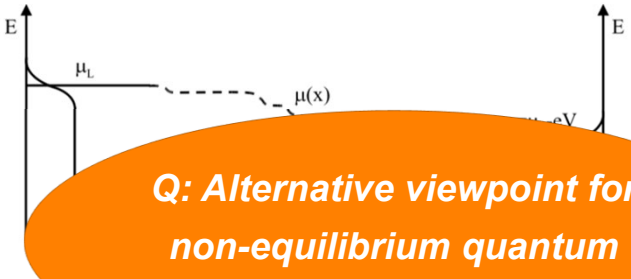




Rolf William Landauer
(1927~1999)

Q: Alternative viewpoint for non-equilibrium quantum transport calculations???

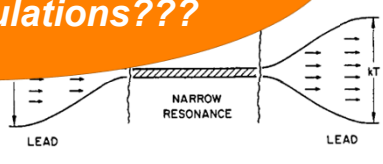
- Landauer "condition": ∃ *reservoirs*

$$\mathcal{E} = \boldsymbol{E} - \nabla\bar{\mu}/e$$

→ *Drift* → *Diffusion*

$$\Delta\mu(\boldsymbol{r},t) = e\,\Delta\phi(\boldsymbol{r},t) + \Delta\bar{\mu}(\boldsymbol{r},t)$$

Electrochemical potential | *Electrostatic potential* | *Chemical potential*



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R. Landauer, *Phys. Scr.* **T42**, 110 (1992)
Y. Imry & R. Landauer, *Rev.Mod. Phys.* **71**, S306 (1999)

Outline

I. Beyond DFT-NEGF? → Beyond Landauer "viewpoint"

II. Multi-space excitation viewpoint → MS-DFT

- Formulation → Total energy
- Voltage drop: Quasi-Fermi level splitting & Landauer resistivity dipole
- Graphene vertical vdW tunneling transistor & NDR

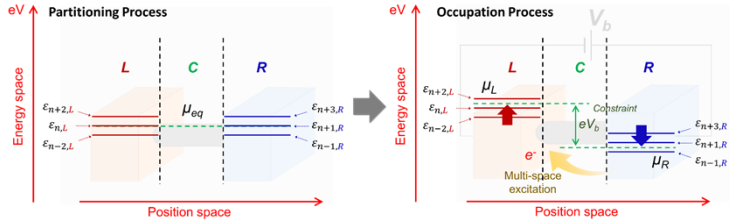
III. Summary

Alternative to Landauer & 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

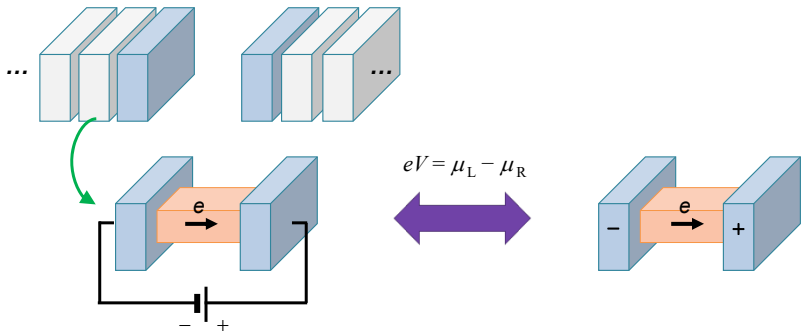
- H.S. Kim & YHK, arXiv [cond-mat.mes-hall], 1808.03608 (2018)
- J. Lee, H. Yeo, & YHK, PNAS **117**, 10142 (2020)
- T.H. Kim, J. Lee, R.-G. Lee, & YHK, Adv. Sci. **7**, 2001038 (2020)

Multi-Space constrained-search DFT: Formulation

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

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

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



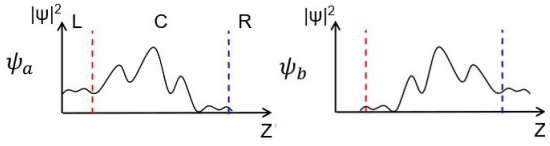
"battery" → current *"capacitor" → current*

MS-DFT: Formulation – Step 2

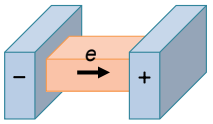
*Quantum **transport** = Multi-space (space-discriminating) **excitation***
→ Variational DFT calculation of steady-state current

Step 2. Assign Ψ to *L*, *C*, & *R* regions

"locality" or "near-sightness" in C (semi-conductors)
(W. Kohn)



$$\psi_i(\vec{r}) \in \begin{cases} \psi_i^L \text{ if } \int_L |\psi_i(\vec{r})|^2 d^3r > \int_{C/R} |\psi_i(\vec{r})|^2 d^3r, \\ \psi_i^C \text{ if } \int_C |\psi_i(\vec{r})|^2 d^3r > \int_{L/R} |\psi_i(\vec{r})|^2 d^3r, \\ \psi_i^R \text{ if } \int_R |\psi_i(\vec{r})|^2 d^3r > \int_{L/C} |\psi_i(\vec{r})|^2 d^3r \end{cases}$$



- $V = 0 : \rho_0(\vec{r}) = \rho_0^L(\vec{r}) + \rho_0^C(\vec{r}) + \rho_0^R(\vec{r})$
- $V \neq 0: \ \rho_k(\vec{r}) = \rho_k^L(\vec{r}) + \rho_k^C(\vec{r}) + \rho_k^R(\vec{r})$

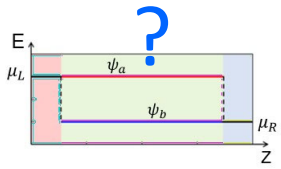
MS-DFT: Formulation – Step 3

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



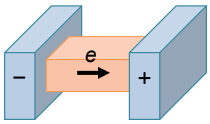
For the "excited" state k;

$$E_k = \min_\rho \left\{ \int v(\vec{r})\,\rho(\vec{r}) d^3\vec{r} + F\left[\rho_k^L, \rho_k^C, \rho_k^R, \rho_0\right] \right\}$$
$$= \int v(\vec{r})\,\rho(\vec{r}) d^3\vec{r} + F[\rho_k, \rho_0]$$

with (*orthogonal*)

$$F[\rho_k, \rho_0] = \min_{\Psi^{L/C/R} \to \rho_k} \langle \Psi_{L/C/R} | \hat{T} + \hat{V}_{ee} | \Psi_{L/C/R} \rangle$$

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



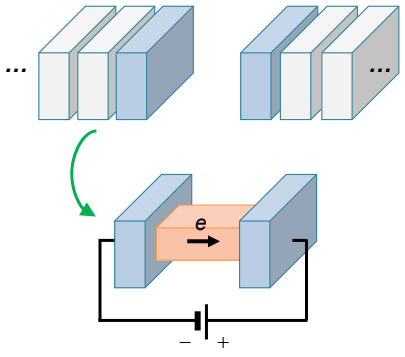
$$\rho_k(\vec{r}) = \rho_k^L(\vec{r}) + \rho_k^C(\vec{r}) + \rho_k^R(\vec{r})$$

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):
  $T(E;V) = Tr\left[\Gamma_L G \Gamma_R G^\dagger\right]$
- Finite electrodes:
  $T(E;V) = Tr\left[\mathrm{A}_L M \mathrm{A}_R M^\dagger\right]$ with $M = \tau_L^+ G \tau_R$
- I-V:
  $I(V) = \frac{e}{h}\int_{-\infty}^{\infty} dE\; T(E;V)\,[f_1(E) - f_2(E)]$



MS-DFT: Kohn-Sham scheme

N.B. "Current" is not our simulation target any more.
→ Instead, minimizing "energy" within the "constraint $eV = \mu_1 - \mu_2$"

0. Applied bias as a constraint: $eV = \mu_1 - \mu_2$
1. Assign ψ_i to L/C/R (multi-space) regions
2. Minimize energy functional via constrained search :

$$E_k = \min_\rho \left\{ \int v(\vec{r})\,\rho(\vec{r}) d^3\vec{r} + F\left[\rho_k^L, \rho_k^C, \rho_k^R, \rho_0\right] \right\} \quad \text{(total energy)}$$

$$F[\rho_k, \rho_0] = \min_{\Psi^{L/C/R} \to \rho_k} \left\langle \Psi_{L/C/R} \middle| \hat{T} + \hat{V}_{ee} \middle| \Psi_{L/C/R} \right\rangle \quad \text{(universal functional)}$$

$\Rightarrow$ Solve (non-equilibrium) Kohn-Sham (KS) equations

$$\left[\hat{h}_{KS}^0 + \Delta v_{Hxc}(\vec{r})\right]\psi_i(\vec{r}) = \varepsilon_i\,\psi_i(\vec{r})$$

MS-DFT: Summary & Implementation

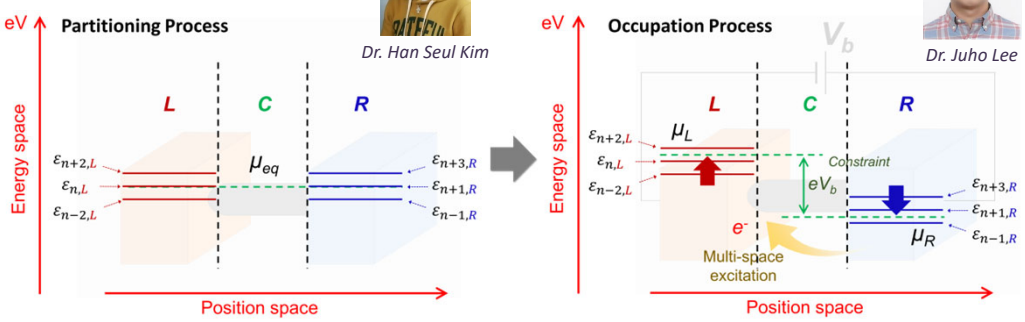
*Quantum **transport** = Multi-space (space discriminating) **excitation***
→ Variational constrained-search DFT calculation of quantum transport



Dr. Han Seul Kim

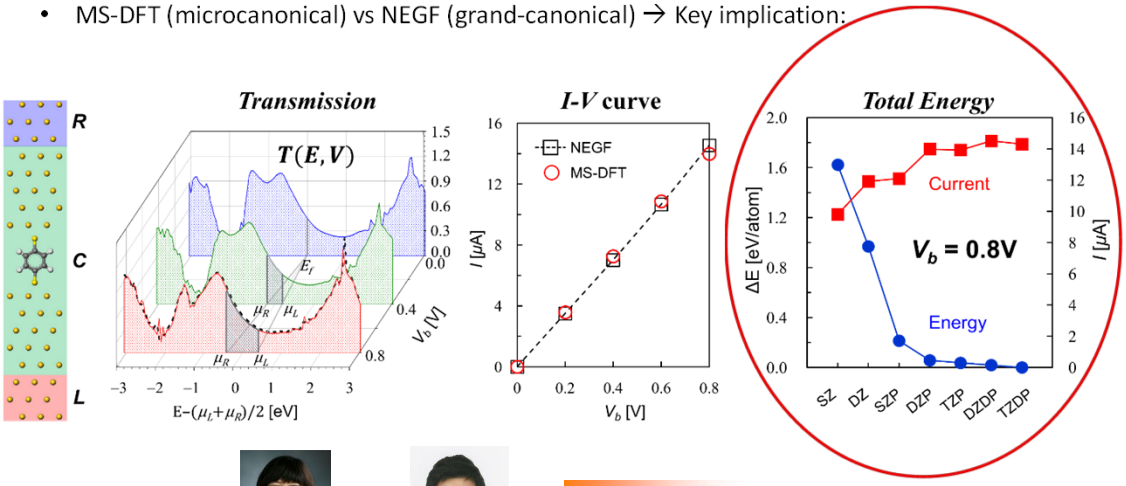


Dr. Juho Lee



MS-DFT advantage 1. "Non-equilibrium" total energy

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





Dr. Han Seul Kim



Dr. Juho Lee

J. Lee, H. Kim, & YHK, Adv. Sci. **7**, 2001038 (2020)

2. Quasi-Fermi levels (Electrochemical potential drop)

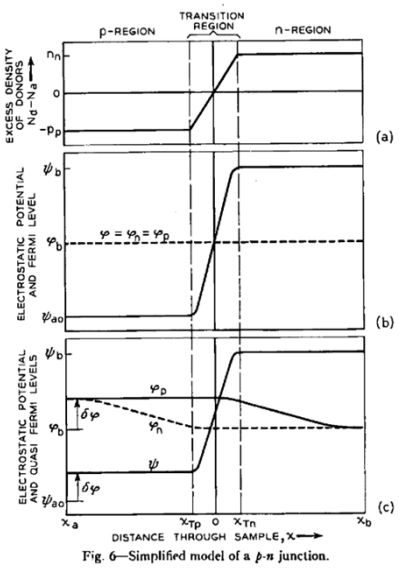
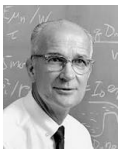


Fig. 6—Simplified model of a *p-n* junction.



William Shockley (1910~1989)



Nobel Prize in Physics 1956

- ***p-n junction***

  Shockley, Bell Sys. Tech. J. **28**, 435 (1949)

- ***e-h recombination***

  Shockley-Read, Phys. Rev. **87**, 835 (1952)

- ***Solar cell***

  Shockley-Queisser, J. Appl. Phys. **32**, 510 (1961)

N.B.

After 70 years since its inception,

NO 1st-principles calculations of QFLs

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

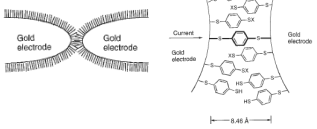
e.g. Molecular electronic devices

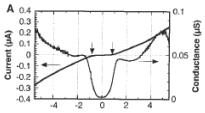


Mark Reed
(1955~2021)

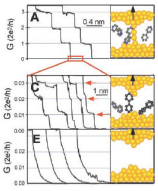


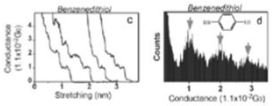
Nongjian Tao
(1963~2020)



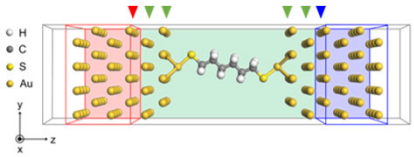


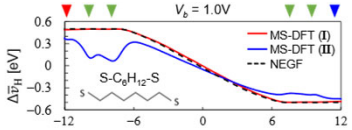
Science (1997)



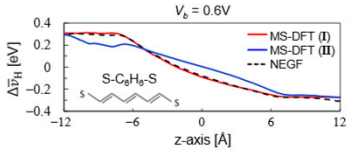


Science (2003)





Hexane-dithiolate



Hexatriene-dithiolate

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

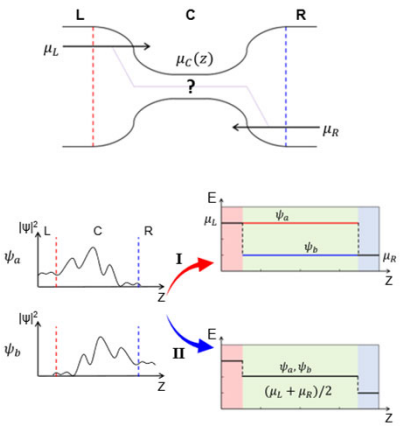
- Occupation rule? → Important to maintain the separate (non-local) QFLs!



Juho Lee

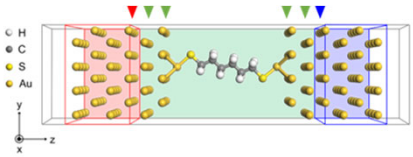


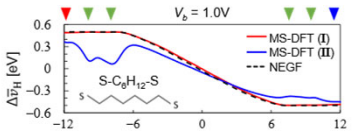
Hyun Woo Yeo



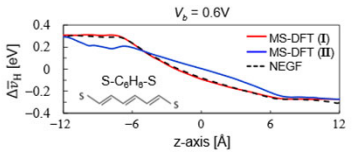
J. Lee, H. Yeo, & YHK, PNAS **117**, 10142 (2020)

$$cf.\quad n(\vec{r}) = \frac{1}{2\pi}\int_{-\infty}^{+\infty} dE\,\mathbf{G}^{n}(\vec{r},E) \approx \frac{1}{2\pi}\int_{-\infty}^{+\infty} dE\,[\underbrace{f_1\mathbf{A}_1}_{\mathbf{G}\Gamma_1\mathbf{G}^+} + \underbrace{f_2\mathbf{A}_2}_{\mathbf{G}\Gamma_2\mathbf{G}^+}]$$





Hexane-dithiolate



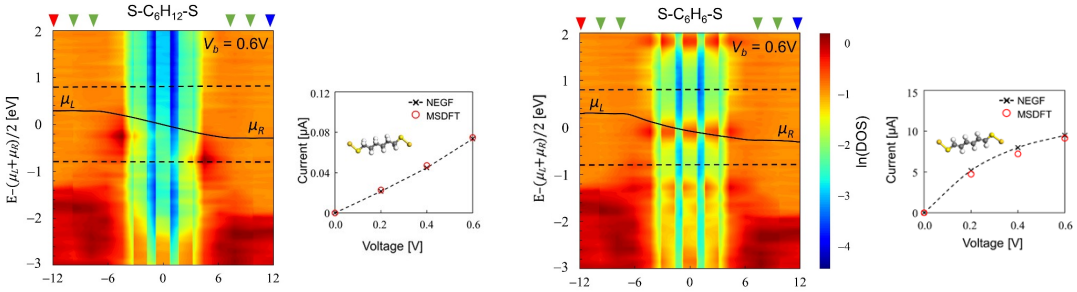
Hexatriene-dithiolate

$$\psi_i(\vec{r}) \in \begin{cases} \psi_i^{L} \text{ if } \int_{L} |\psi_i(\vec{r})|^2 d^3r > \int_{C/R} |\psi_i(\vec{r})|^2 d^3r, \\ \psi_i^{C} \text{ if } \int_{C} |\psi_i(\vec{r})|^2 d^3r > \int_{L/R} |\psi_i(\vec{r})|^2 d^3r, \\ \psi_i^{R} \text{ if } \int_{R} |\psi_i(\vec{r})|^2 d^3r > \int_{L/C} |\psi_i(\vec{r})|^2 d^3r \end{cases}$$

QFLs: Where is the "voltage" drop?

- Electrostatic potential drop: Why nonlinear drop @ hexatriene-dithiolate?

Hexane-dithiolate **(insulator)** **Hexatriene-dithiolate** **(semiconductor)**



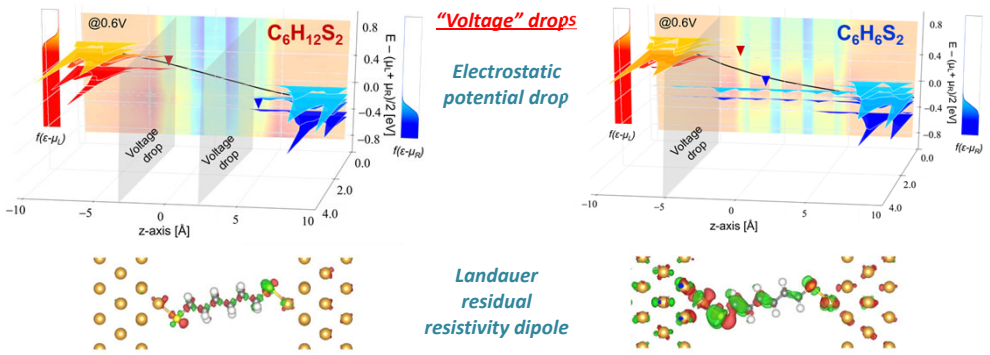
Electrochemical potential drop

$$V = \int_{r_1}^{r_2} \mathcal{E} \cdot d\boldsymbol{r} = \frac{\mu_1(\boldsymbol{r}_2) - \mu_1(\boldsymbol{r}_2)}{e} = \phi(\boldsymbol{r}_2) - \phi(\boldsymbol{r}_1) + \frac{\bar{\mu}(\boldsymbol{r}_2) - \bar{\mu}(\boldsymbol{r}_1)}{e}$$

Electrostatic potential drop *Chemical potential drop*

Electrostatic potential drops

Hexane-dithiolate **Hexatriene-dithiolate**



"Voltage" drops

Electrostatic potential drop

Landauer residual resistivity dipole

Electrochemical potential drops (QFLs)

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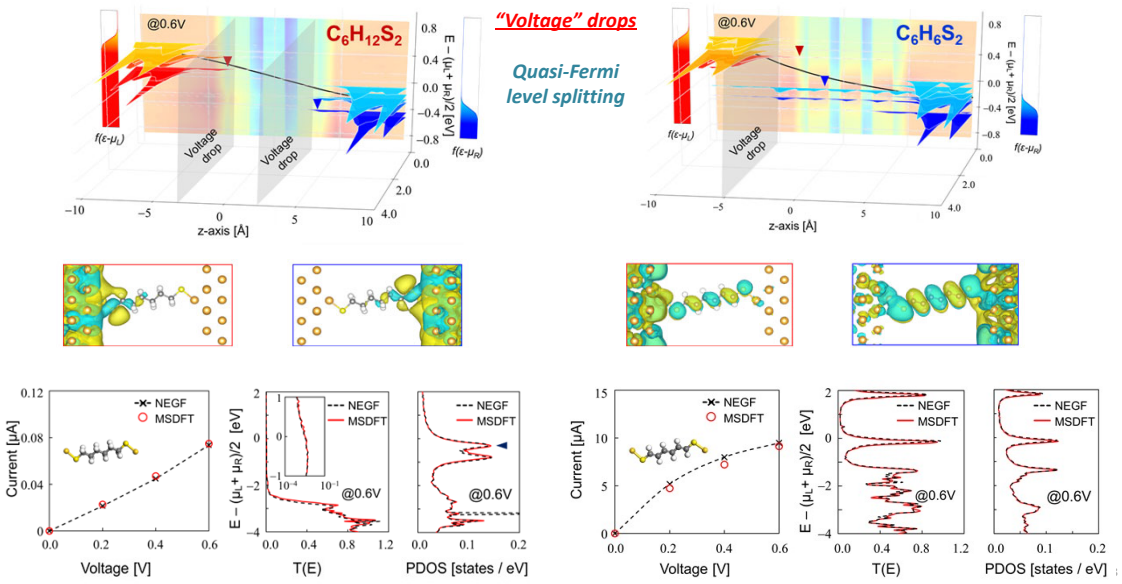
Hexane-dithiolate | **Hexatriene-dithiolate**



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

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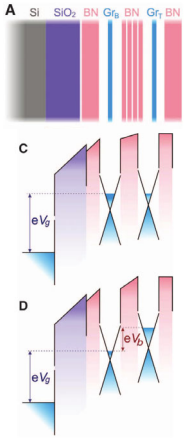
Vertical tunneling field effect transistor (FET)

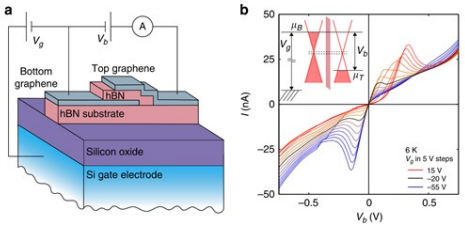
L. Britnell *et al. Science* **335,** 947 (2012)



Modulation of tunneling currents
→ On/Off ≈ 1×10⁴

- *Negative Differential Resistance (NDR)*

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



- *High photocurrent*

  L. Britnell *et al. Science* 340, 1311 (2013), etc.

- *Chiral quantum states*

  J. Wallbank *et al. Science* 353, 6299 (2016), etc.

- *Giant tunneling magnetoresistance*

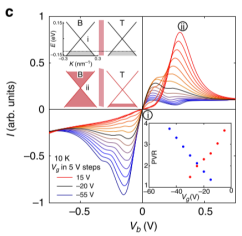
  T. Song *et al. Science* 360, 1214 (2018), etc.

- *etc.*

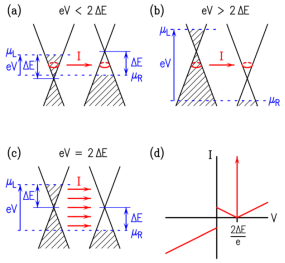
Only semi-classical theory (not NEGF)

- Semi-classical Bardeen approach

$$I = g_V \frac{4\pi e}{\hbar} \sum_{\alpha,\beta} |M_{\alpha\beta}|^2 \left[f_L(E_\alpha) - f_R(E_\beta) \right] \delta(E_\alpha - E_\beta)$$

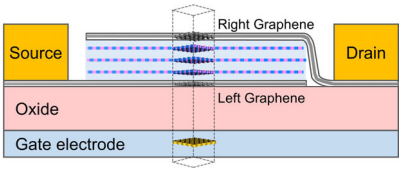


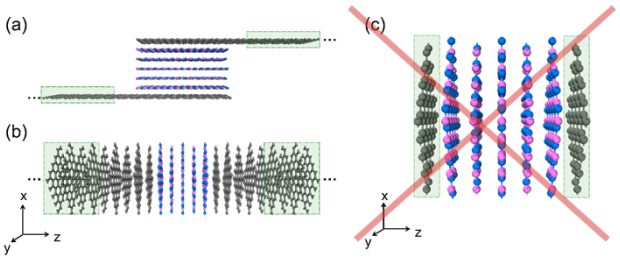
L. Britnell *et al.*
Nat. Commun. **4,** 1794 (2013)



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

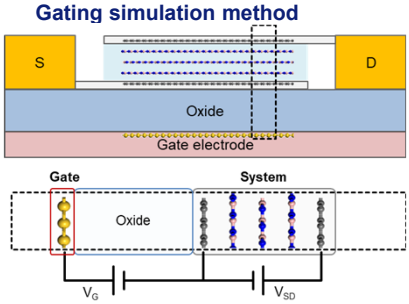
- Difficulty with DFT-NEGF





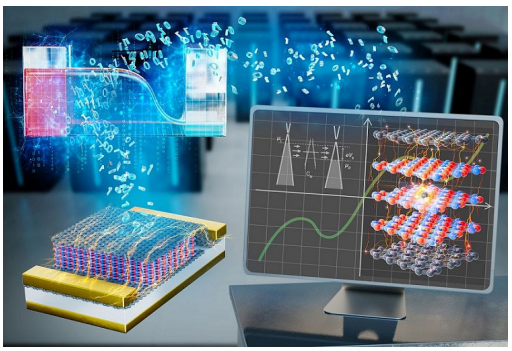
MS-DFT for graphene tunneling "FET"

Gating simulation method



1. "Constrained search":
   V_G as a constraint that precedes V_{SD}
2. Transmission:

$$T(E; V_b, V_g) = Tr\left[\boldsymbol{a}_L \, \mathbf{M} \, \boldsymbol{a}_R \, \mathbf{M}^\dagger \right]$$



T.H. Kim, J. Lee, R.-G. Lee, & YHK,
Npj Comput. Mater. **8,** 50 (2022)

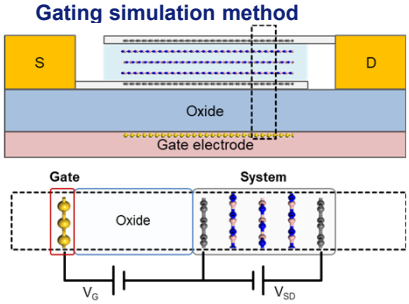

Taehyung Kim


Juho Lee


Ryong Gyu Lee

MS-DFT for graphene tunneling "FET"

Gating simulation method



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2. Transmission:
   $T(E; V_b, V_g) = Tr[\boldsymbol{a}_L \, \mathbf{M} \, \boldsymbol{a}_R \, \mathbf{M}^\dagger]$

"Gate-versus defect-induced voltage drop & negative differential resistance in vertical graphene heterostructures"

- "Voltage" drop?

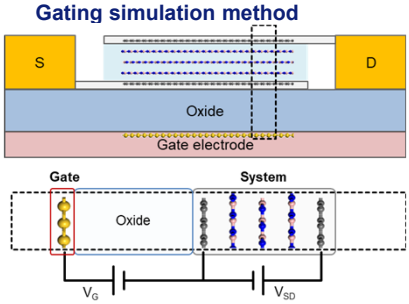
  Electrochemical potential drop

$$V = \int_{r_1}^{r_2} \mathcal{E} \cdot d\boldsymbol{r} = \frac{\mu_1(\boldsymbol{r}_2) - \mu_1(\boldsymbol{r}_2)}{e}$$
$$= \phi(\boldsymbol{r}_2) - \phi(\boldsymbol{r}_1) + \frac{\bar{\mu}(\boldsymbol{r}_2) - \bar{\mu}(\boldsymbol{r}_1)}{e}$$

Electrostatic potential drop — *Chemical potential drop*

MS-DFT for graphene TFET: $V_G = +1V$

Gating simulation method



1. "Constrained search":
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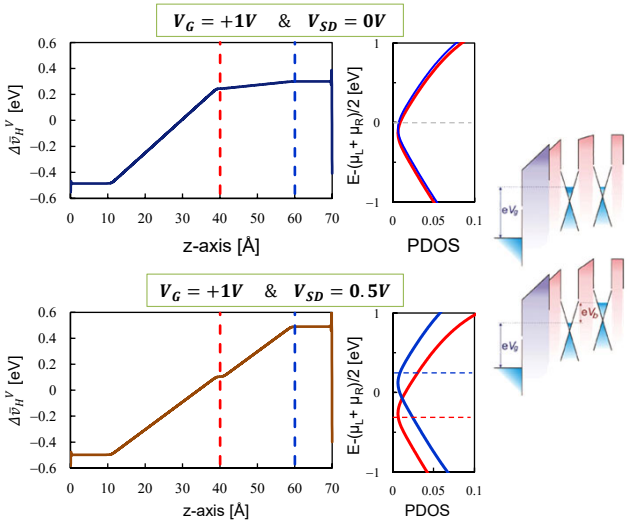
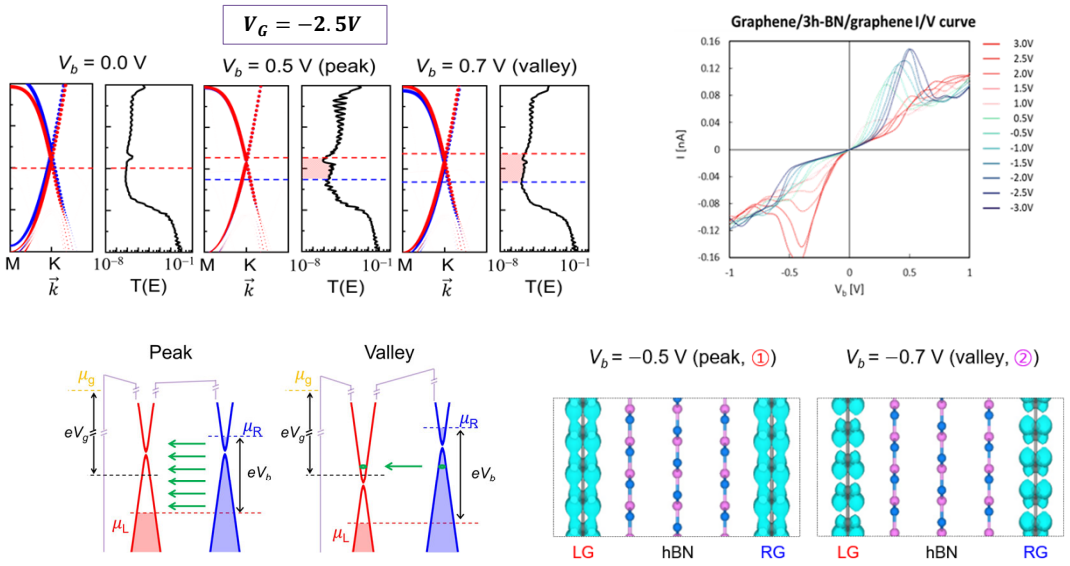
2. Transmission:
   $T(E; V_b, V_g) = Tr[\boldsymbol{a}_L \, \mathbf{M} \, \boldsymbol{a}_R \, \mathbf{M}^\dagger]$

$\Delta\bar{v}_H^V(\vec{r}; V_{SD}, V_G) = \bar{v}^V(\vec{r}; V_{SD}, V_G) - \bar{v}^0(\vec{r}; 0, 0)$

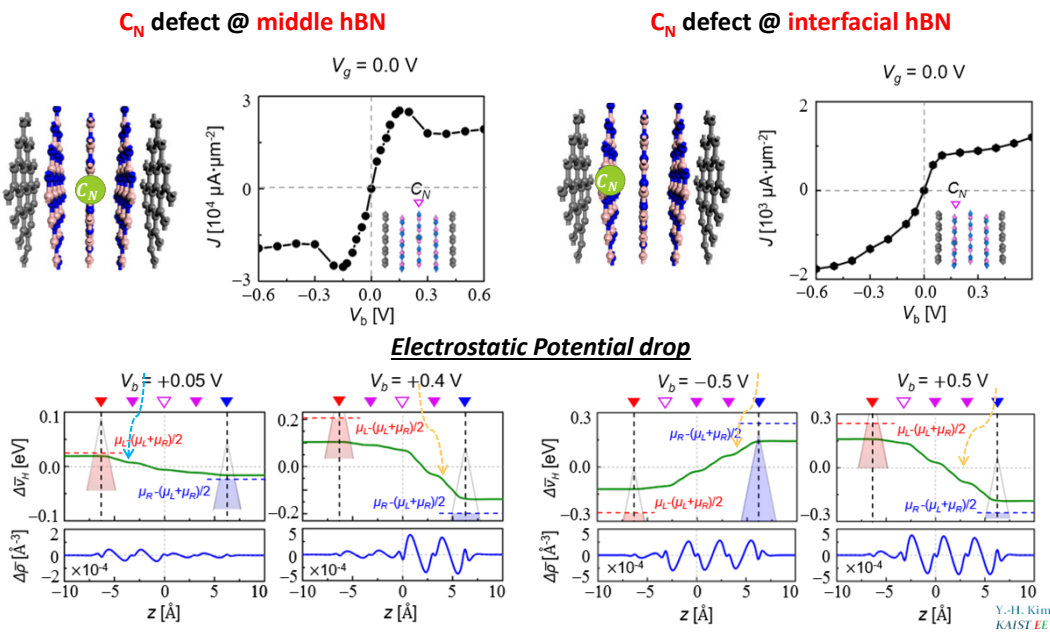


- Quantum capacitance → Field partial penetration

NDR @ Gr/pristine hBN/Gr TFET ← MS-DFT



Gr/defective hBN/Gr: I-V & voltage drop



Gr/defective hBN/Gr: C_N @ interfacial hBN → No NDR

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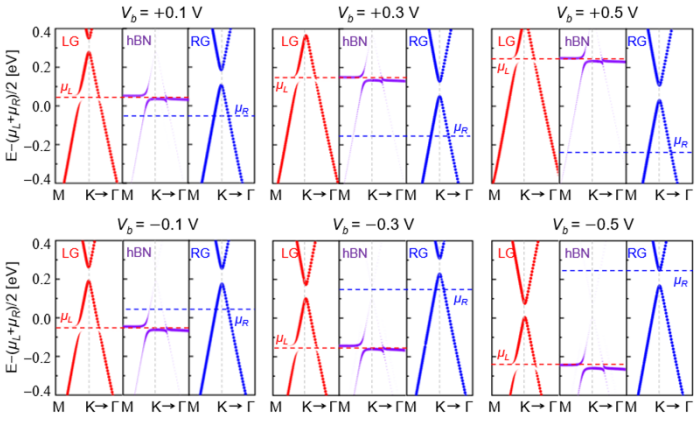

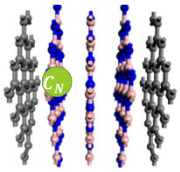

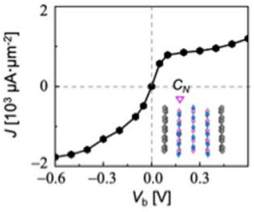

- Pinning of C_N defect @ left Gr

Gr/defective hBN/Gr: C_N @ middle hBN → symmetric NDR

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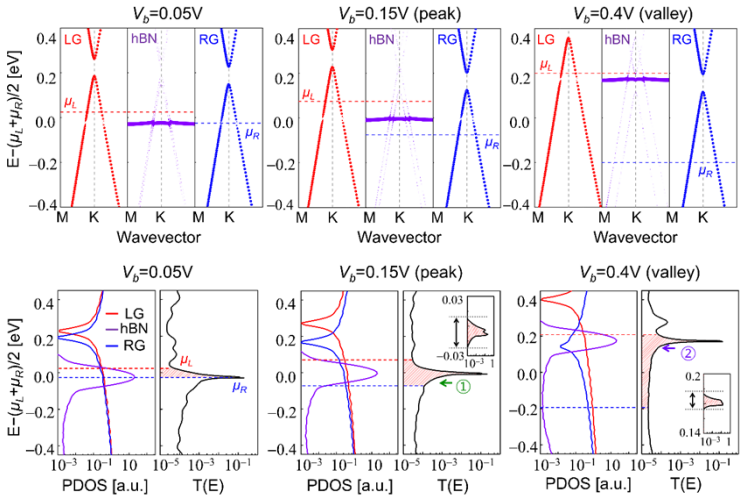

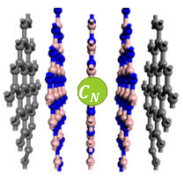

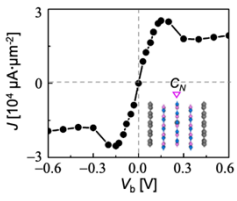

- Self-consistent filling of C_N defect levels → upshift with V_b
- C_N defect level-mediated symmetric NDR

Gr/defective hBN/Gr: C_N @ middle hBN → QH-NDR

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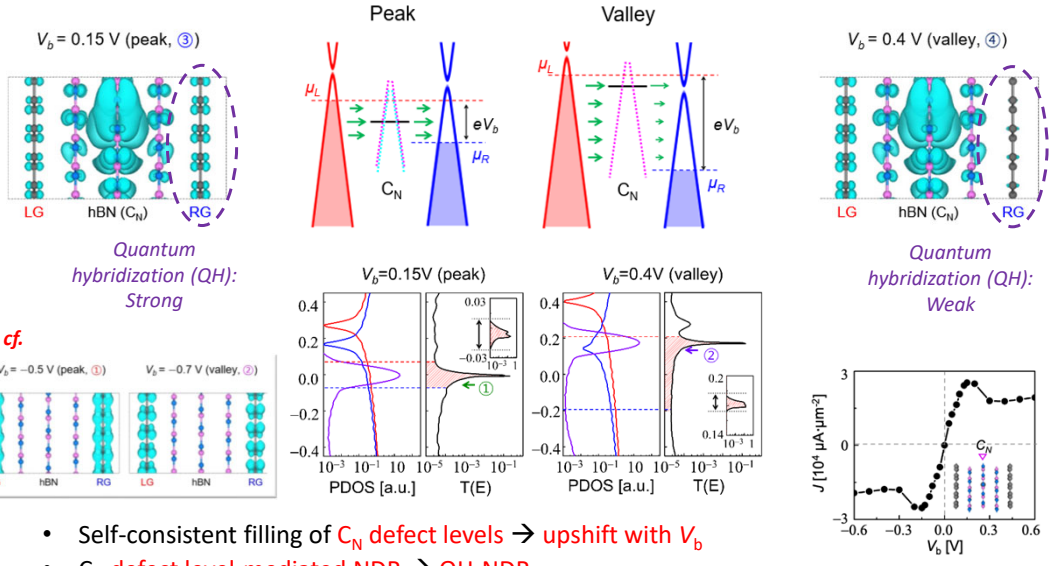


- Self-consistent filling of C_N defect levels → upshift with V_b
- C_N defect level-mediated NDR → QH-NDR

Outline

전자구조계산 겨울학교 2023. 1. 20

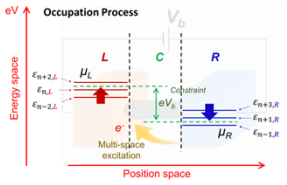
I. Background information: DFT, NEGF, & Landauer

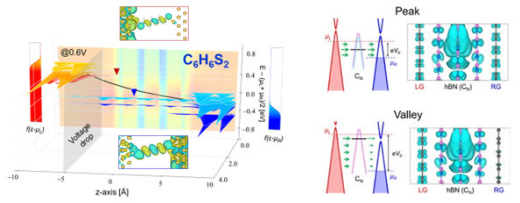
II. MS-DFT: development & its applications

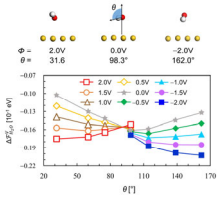
III. Summary & Outro

Summary: Lecture 3

- Importance of “picture” or “viewpoint”
- “Multi-space excitation” viewpoint for quantum transport
  - An alternative to the Landauer viewpoint
  - Formulation of MS-DFT (vs. DFT-NEGF)
- Advantages and Applications
  - Quasi-Fermi levels: “Voltage drop”
  - Graphene-based nanodevices
  - Total energy
  - → Electric enthalpy (of formation)
  - → Interfacial water (and beyond …)







Acknowledgements

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http://nanocore.kaist.ac.kr/yhklab

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- Ms. Hyo Jin Jeon

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- **Dr. Han Seul Kim**

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- Jaeun Kim
- Jiyoon Song



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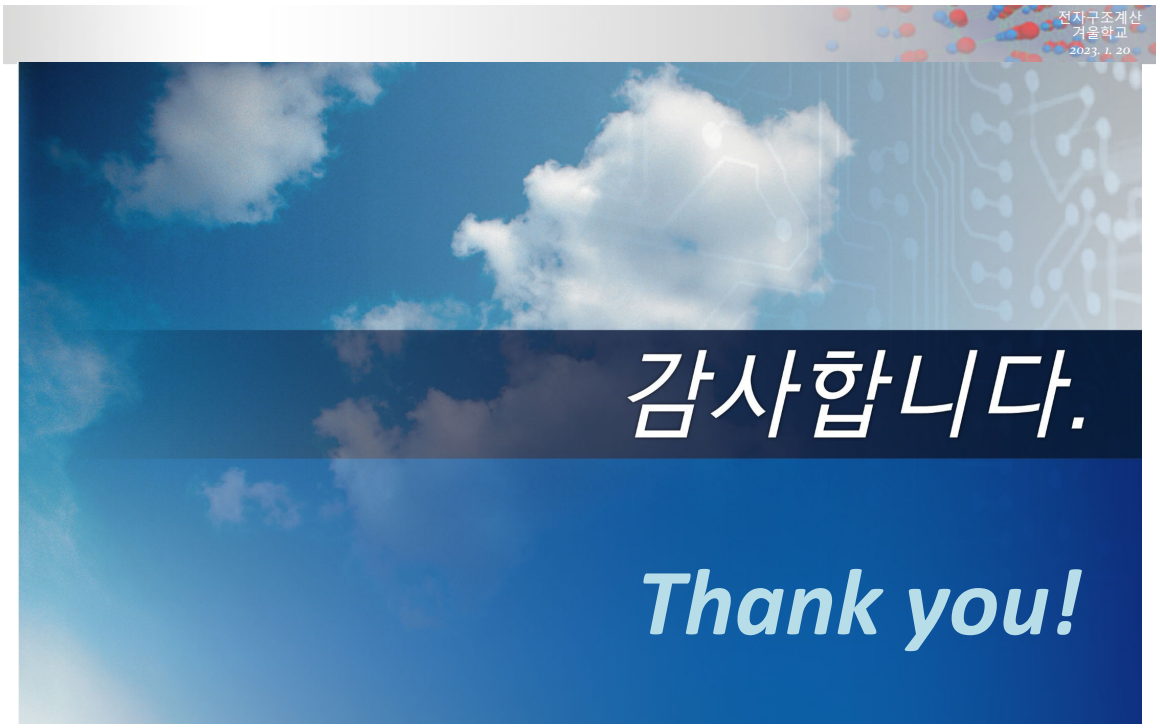
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겨울학교
2023. 1. 20
감사합니다.
Thank you!