Projector-based Electron Transport Calculations

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August 15, 2018

Outline

- Overview of Research
- Problems in Existing Transport Calculations
- Proposed Method
- Software Development

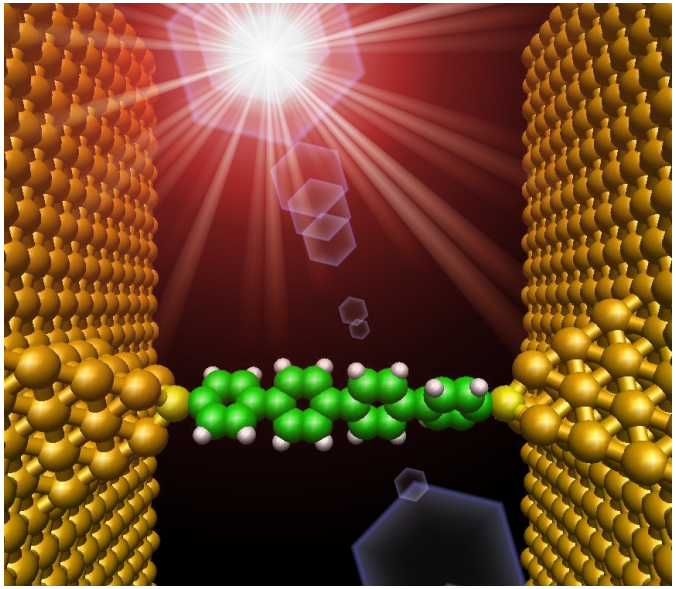
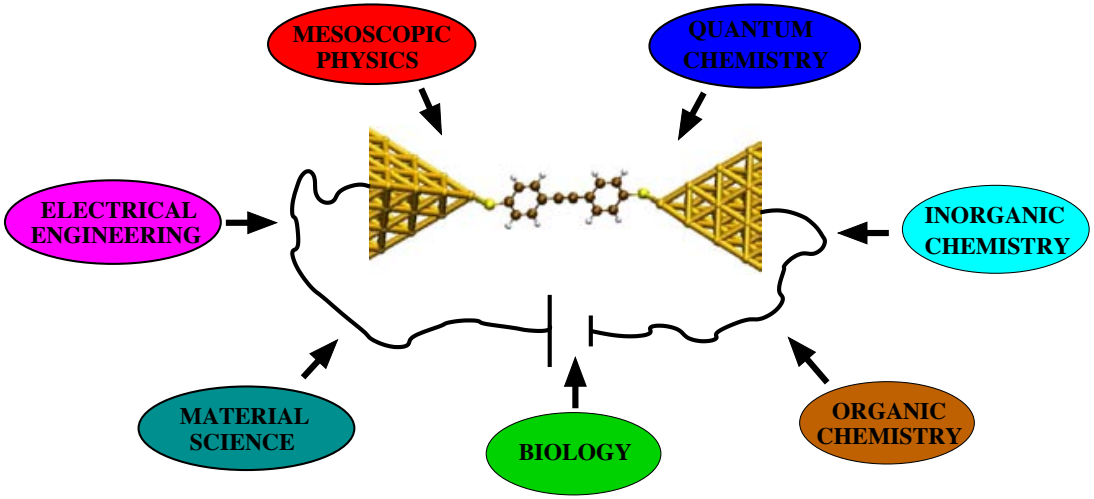


Figure from ref. [1]

Electron Transport Through Molecular Junctions



Why molecular electronics?

1) Fundamental science: Explore properties of materials at molecular scale

2) Technological applications: Offer advantages over silicon-based technology

- Size ↓
- Speed ↑
- Assembly & recognition
- New functionalities

Figure from ref. [1]

Problems in Existing Transport Calculations

Discrepancies between calculations and experimental data:

- good qualitative agreement
- but overestimation !

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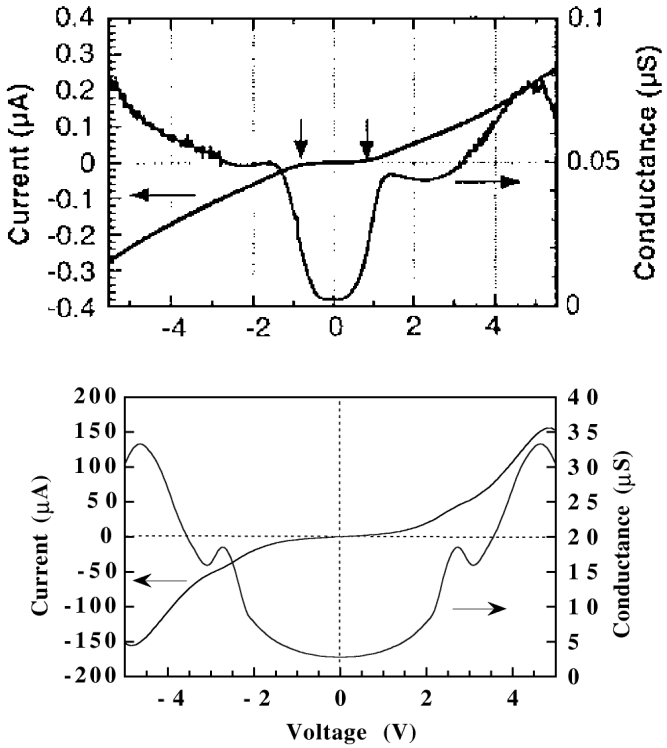

FIG. 2. Top: Experimental *I-V* characteristic of a benzene-1,4-dithiolate molecule measured by Reed *et al*. [1]. Bottom: Conductance of the molecule of Fig. 1 as a function of the external bias applied to the metallic contacts.

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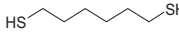
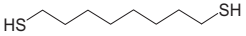
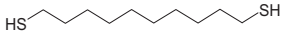
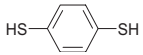
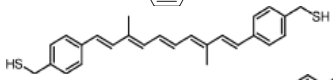
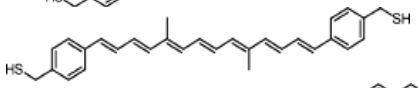
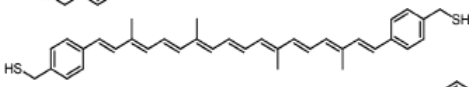
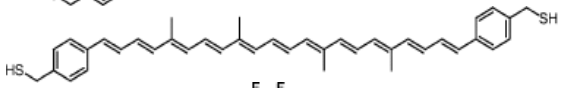
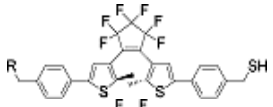
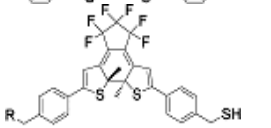
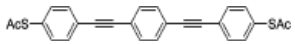
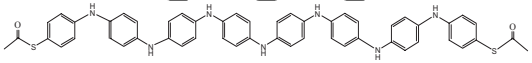
	Molecule	*G* (measured) [nS]	*G* (theoretical) [nS]	Ratio
1		95 ± 6	185	0.51
2		19.6 ± 2	25	0.78
3		1.6 ± 0.1	3.4	0.47
4		833 ± 90	47 000	0.02
5		2.6 ± 0.05	7.9	0.33
6		0.96 ± 0.07	2.6	0.36
7		0.28 ± 0.02	0.88	0.31
8		0.11 ± 07	0.3	0.36
9		1.9 ± 3	0.8	2.4
10		250 ± 50	143	1.74
11		~13	190	0.07
12		0.32 ± 0.03	0.043	7.4

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- K. Stokbro, J. Taylor, M. Brandbyge, J.-L. Mozos & P. Ordejon, Comp. Mat. Sci. **27**, 151-160 (2003)
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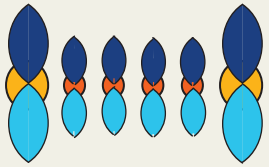
Speculations: - experimental limitations
- inadequate treatment of electron correlation
- numerical artifacts

Ghost Transmission

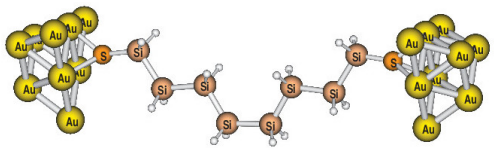
- Key quantity in electron transport is the transmission function T(E).
- Herrmann and colleagues[2] carried out two types of transport calculations:

"full" calculation



"ghost" calculation

- They saw artificially high transmission (named *ghost transmission*) in the ghost system.



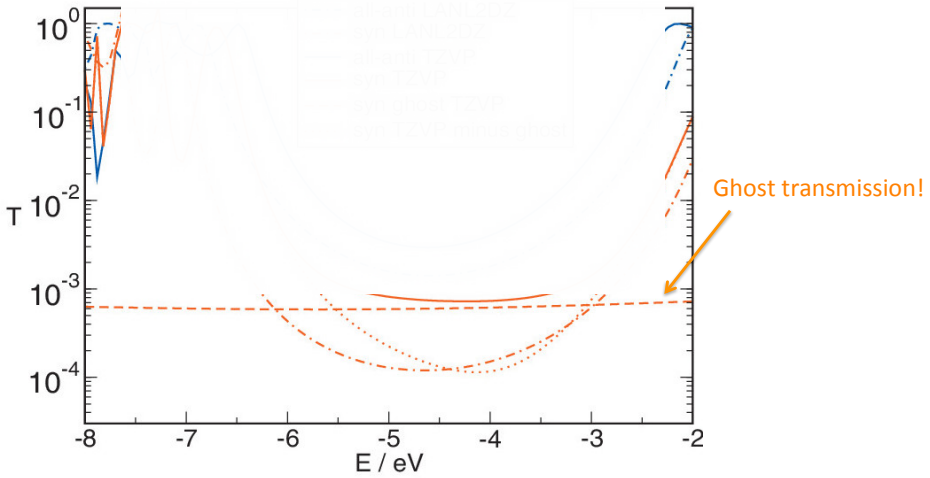
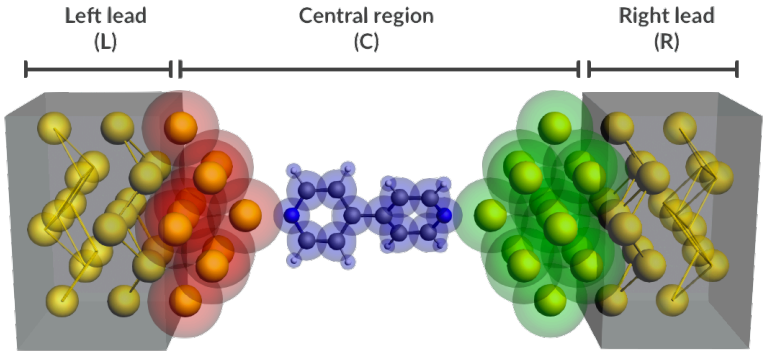


Figure (ref.[2]): Transmission for octasilane-dithiolate chain

Electron Transport Calculations



The standard approach to first-principles calculations consists of two steps:

Electronic Structure Calculation → **Calculation of Transmission Function**

- Density-functional theory (DFT)
- Output needed are
  - Hamiltonian matrix H
  - Overlap matrix S

$$H = \begin{array}{c|ccc} & L & C & R \\ \hline L & & V_L & \\ C & V_L^\dagger & H_C & V_R^\dagger \\ R & & V_R & \end{array}$$

- Landauer-Büttiker theory and non-equilibrium Green's function (NEGF) technique

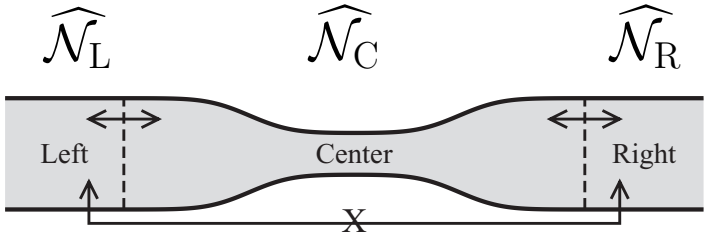
$$\mathbf{\Gamma}_{\mathrm{L/R}}(E) = i[\mathbf{\Sigma}_{\mathrm{L/R}}(E) - \mathbf{\Sigma}^\dagger_{\mathrm{L/R}}(E)]$$

$$\mathbf{G}(E) = [E\mathbf{I} - \mathbf{H}_C - \mathbf{\Sigma}_{\mathrm{L}}(E) - \mathbf{\Sigma}_{\mathrm{R}}(E)]^{-1}$$

$$T(E) = \mathrm{Tr}\left[\mathbf{\Gamma}_{\mathrm{L}}(E)\mathbf{G}(E)\mathbf{\Gamma}_{\mathrm{R}}(E)\mathbf{G}(E)^\dagger\right]$$

Figure from ref. [3]

Projectors: Conventional vs. Proposed



- Use projectors $\widehat{\mathcal{N}}_{\mathrm{j}}$ to divide the system
- Choice of projectors is important!

Conventional transport calculation

- Uses Mulliken-style projectors, *e.g.*,

$$\widehat{\mathcal{N}}_{\mathrm{C}} = \sum_{j\in \mathrm{C}} \sum_{k} |\varphi_j\rangle \, (\mathbf{S}^{-1})_{j,k} \, \langle \varphi_k|$$

- Depends on basis functions $\{\varphi_j\}$
- Results in non-Hermitian operators
- Causes a short circuit[4]

Proposed transport calculation

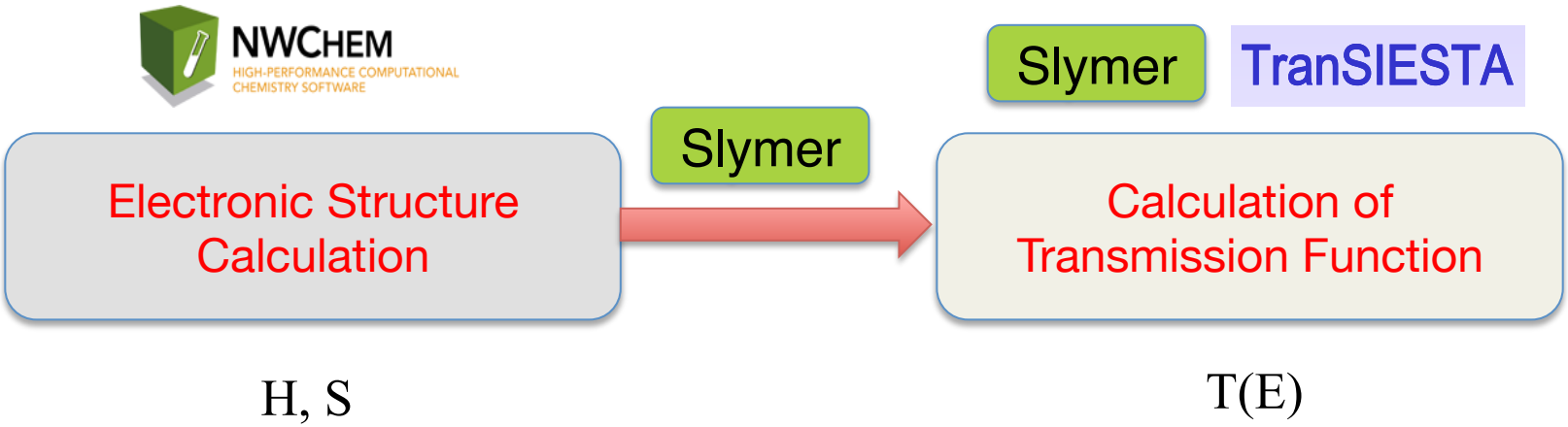
- Uses real-space projectors, *e.g.*,

$$\widehat{\mathcal{N}}_{\mathrm{C}} = \int_{x_-}^{x_+} dx' \int_{-\infty}^{+\infty} dy' \int_{-\infty}^{+\infty} dz' \, |\vec{x}\rangle \, \delta(\vec{x} - \vec{x}') \, \langle \vec{x}'|$$

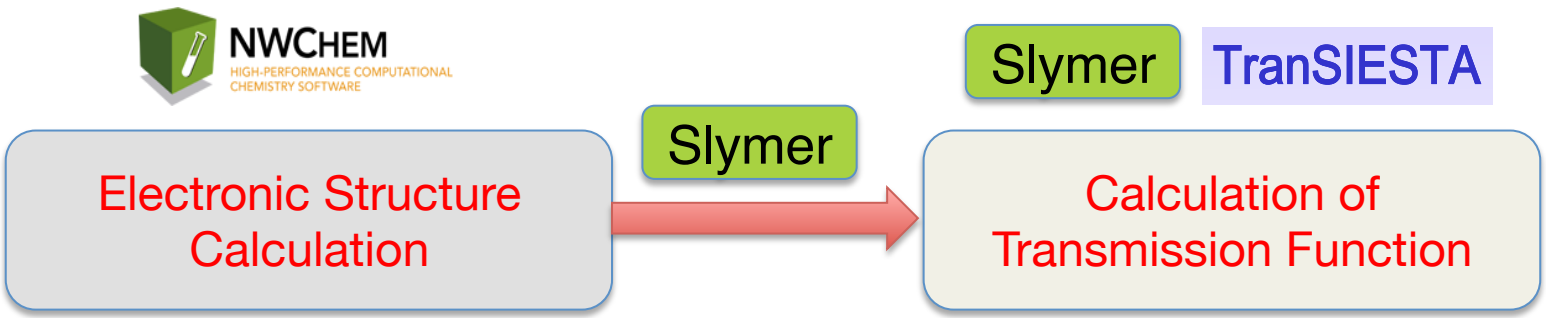
- Does not depend on basis functions
- Results in Hermitian operators
- Does not cause a short circuit[4]

Implementation of Real-Space Projectors

- Goal: develop software that implements real-space projectors
- Slymer[3] = software package from our research group:
  - Acts as a work-around between the 2 steps
  - Can perform electron transport calculation
  - Can do electronic band structure calculation
  - Written in C++



Details of the Calculations



- Create the geometry of molecular junction
- Choose a basis set and the exchange-correlation functional
- Output quantities: **H** and **S**
- Computational bottleneck -> run on a cluster

- Apply projectors to **H** and **S** [Slymer]
- Compute self-energies

$$\mathbf{\Sigma}_{\mathrm{L/R}}(E) = (E\mathbf{S}_{\mathrm{L/R,C}} - \mathbf{V}_{\mathrm{L/R,C}})^{\dagger}\mathbf{g}_{\mathrm{L/R,C}}(E\mathbf{S}_{\mathrm{L/R,C}} - \mathbf{V}_{\mathrm{L/R,C}})$$

- Compute spectral densities

$$\mathbf{\Gamma}_{\mathrm{L/R}}(E) = i[\mathbf{\Sigma}_{\mathrm{L/R}}(E) - \mathbf{\Sigma}^{\dagger}_{\mathrm{L/R}}(E)]$$

- Compute Green's function

$$\mathbf{G}(E) = [E\mathbf{I} - \mathbf{H}_C - \mathbf{\Sigma}_{\mathrm{L}}(E) - \mathbf{\Sigma}_{\mathrm{R}}(E)]^{-1}$$

- Compute transmission function

$$T(E) = \mathrm{Tr}\left[\mathbf{\Gamma}_{\mathrm{L}}(E)\mathbf{G}(E)\mathbf{\Gamma}_{\mathrm{R}}(E)\mathbf{G}(E)^{\dagger}\right]$$

- Compute current and conductance if desired

$$I = \frac{2e}{h}\int_{-\infty}^{\infty}(f_{\mathrm{L}}(E) - f_{\mathrm{R}}(E))T(E)dE$$

$$G = \frac{2e^2}{h}\sum_i T_i$$

Plans to Validate Slymer

- Run calculations for different combinations:

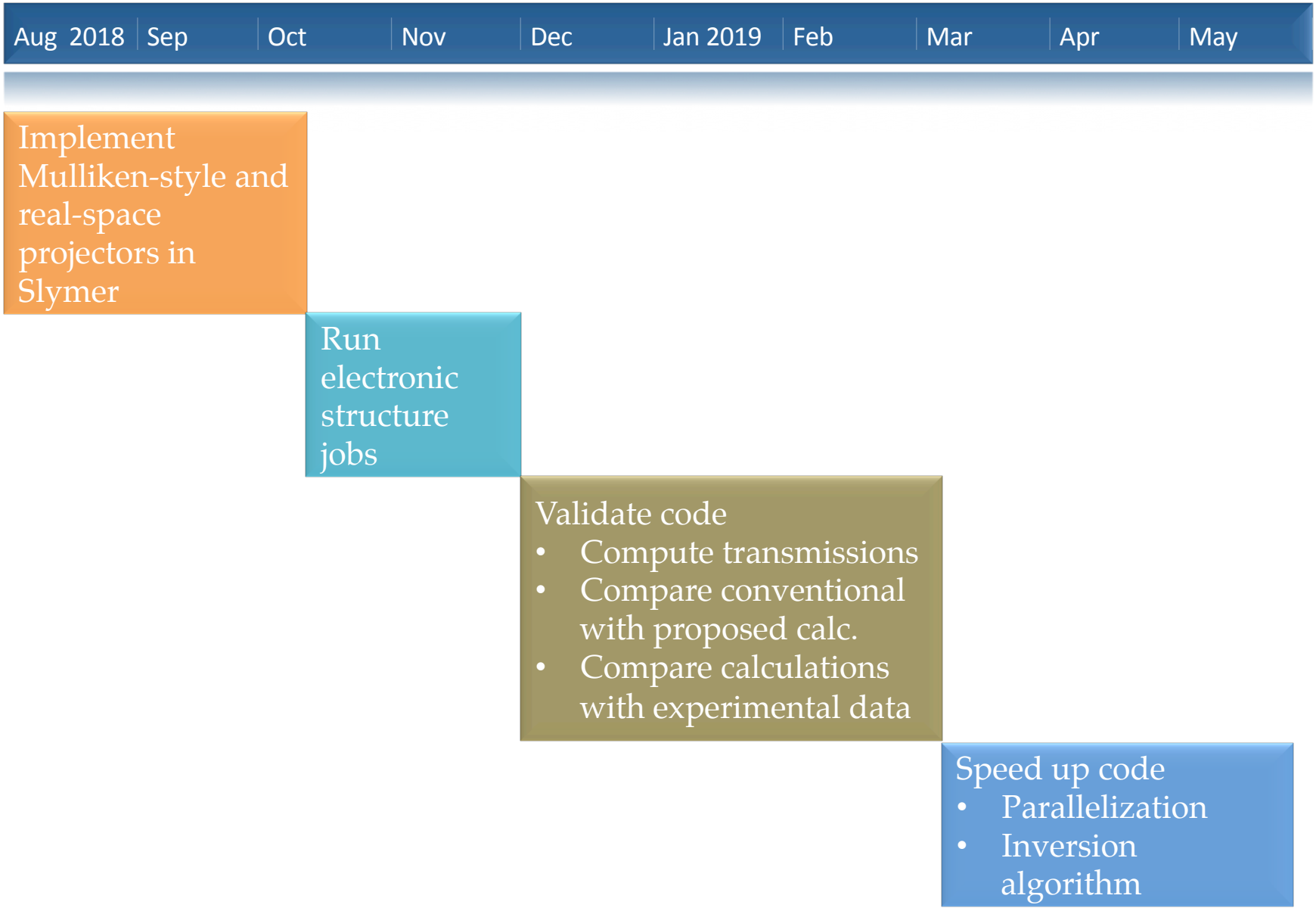
molecule	exchange-correlation functional	basis set
• *meta*-connected benzene • *para*-connected benzene • octane-dithiolate • anthracene derivatives	• LDA[a] • PBE0[b]	• Double-zeta[a] • Triple-zeta[b] • Quadruple-zeta[b]

Note: superscripts a = for prototyping, b = for production

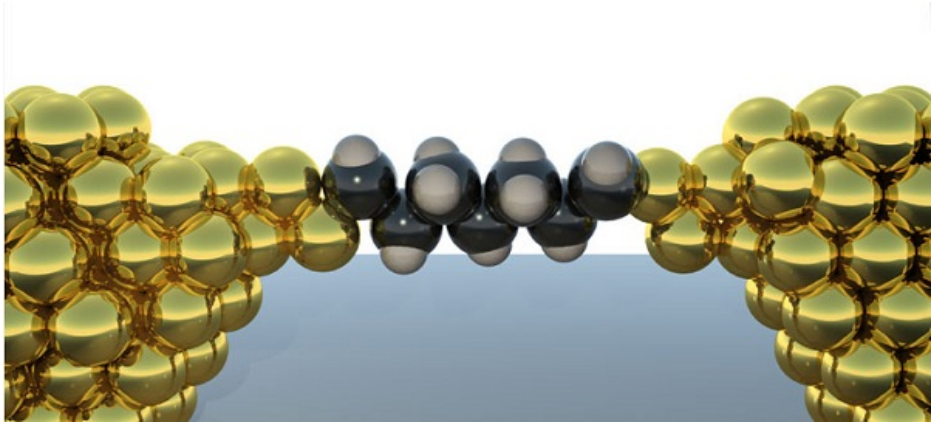
- Compare results: conventional calculations vs. proposed calculations

- Compare our calculations with experiments ➔ collaboration with
  - ➢ Venkataraman Group at Columbia University
  - ➢ Pierre Darancet in Center for Nanoscale Materials at Argonne National Laboratory

Research Timeline



Summary



- Electron transport in molecular junctions has attracted much attention for fundamental science and technological applications.
- Conventional transport calculations (Mulliken-style projectors) lead to ghost transmission and thus overestimation of transport properties.
- We propose using real-space projectors to get rid of ghost transmission.
- Our research group is working on developing a software package named Slymer which implements the proposed transport calculations.
- This implementation will be validated among several molecular junctions.

Figure from ref. [6]

References

[1] Cuevas, Juan Carlos, and Elke Scheer. Molecular Electronics: An Introduction to Theory and Experiment. Vol. 1. World Scientific, 2010.
[2] Herrmann, Carmen, et al. "Ghost transmission: How large basis sets can make electron transport calculations worse." The Journal of chemical physics 132.2 (2010): 024103.
[3] www.scm.com/doc/Tutorials/BAND/NEGF_molecular_junction.html
[4] Reuter, Matthew G., and Robert J. Harrison. "Rethinking first-principles electron transport theories with projection operators: The problems caused by partitioning the basis set." The Journal of chemical physics 139.11 (2013): 114104.
[5] https://github.com/mgr522/slymer
[6] www3.tau.ac.il