You Should Also Think About Complicated Things (to Improve Computation): Exorcising Numerical Ghosts from Electron Transport Calculations

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Oak Ridge National Laboratory
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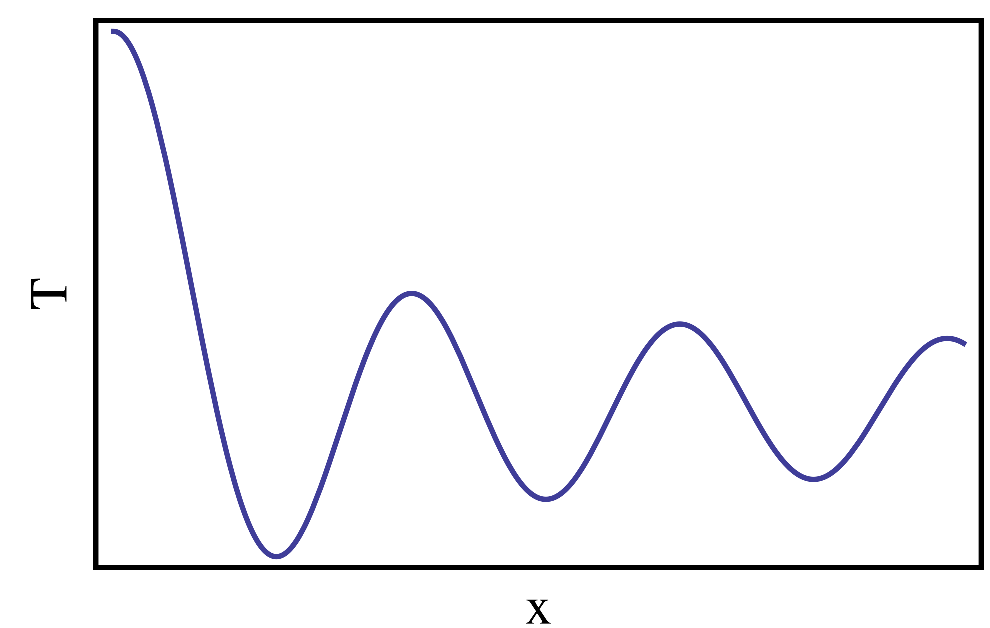
Wigner Fellowship Program

A Motivational Analogy

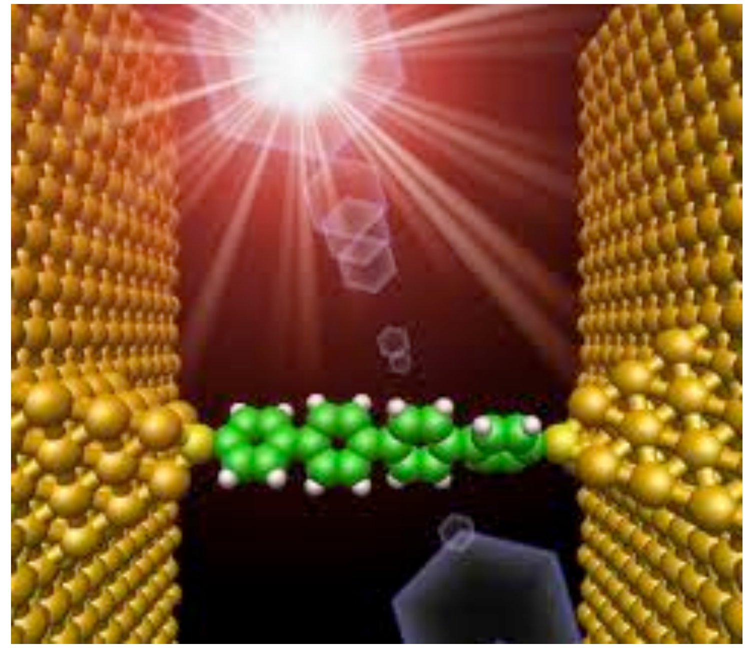
- Suppose a computational model for heat conduction
  - Widely used
  - Provides legitimate answers for a host of problems
- A shrewd student runs a simple test...
  - 1D bar
  - Both ends at the same temperature, no heat source
  - Something's wrong
    - Code? Test? Model?
- Analogy for ghost transmission



Outline

- Electron transport in quantum systems
  - Overview & computational challenges
  - Comparison with “classical” conduction
- Illustrative examples
  - Ghosts do exist! (Ghost transmission)
  - Building a proton pack
  - Exorcising ghost transmission
- Future directions

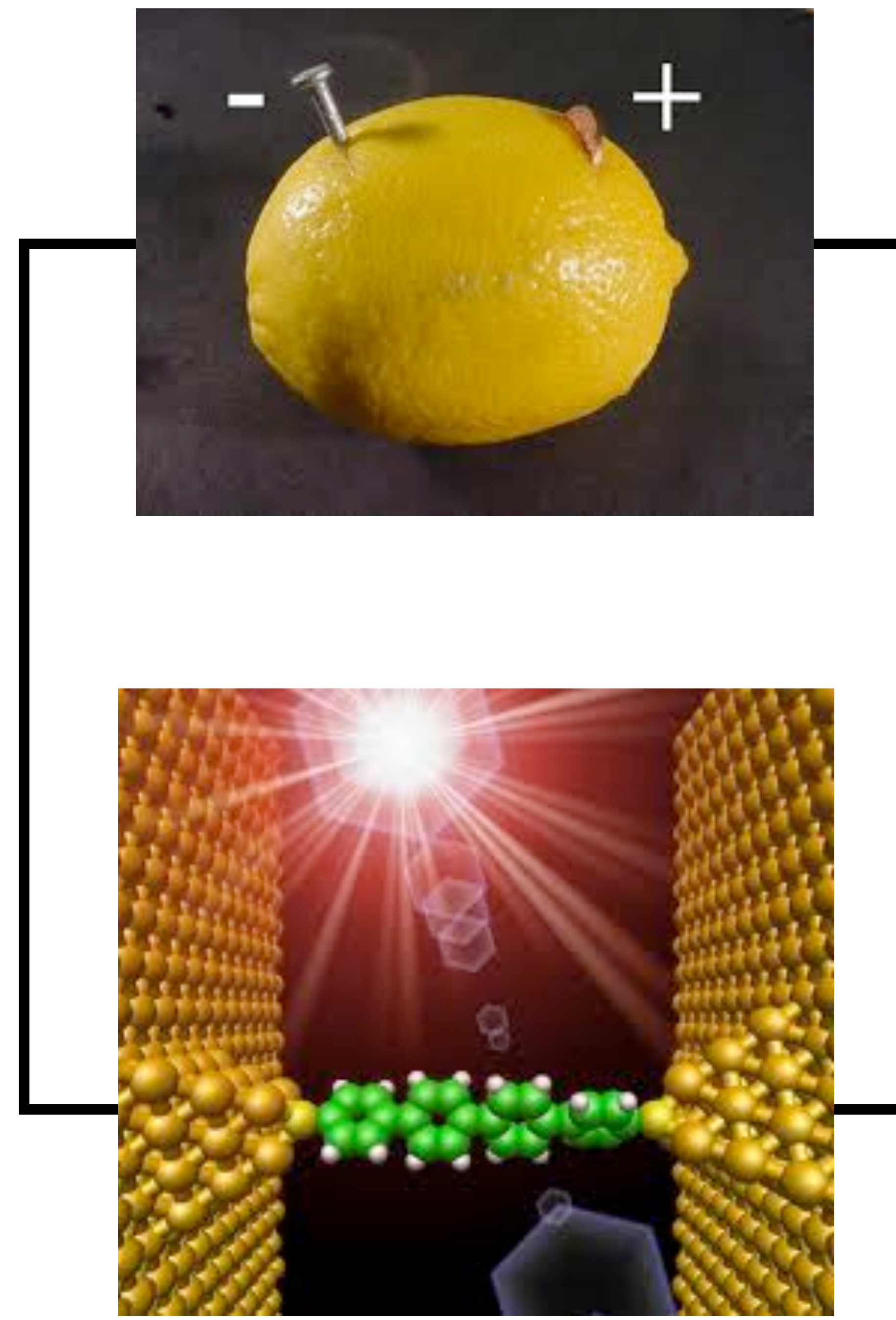
Electron Transport



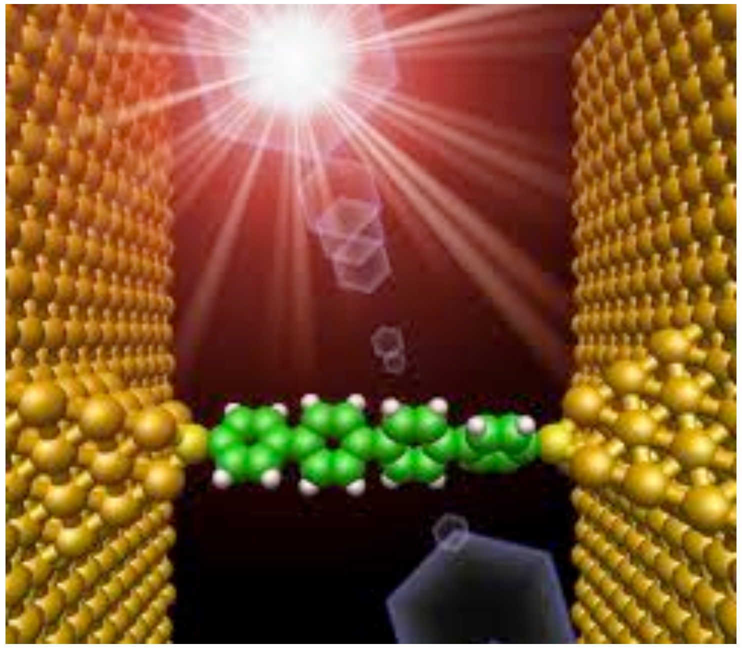
- How does current traverse a **quantum** system?
- Molecular electronics: What is the conductance of a single molecule?
  - How does the conductance scale to multiple wires?
- Fundamentals: Charge transfer / transport
  - Analytical microscopies, solar cells, catalysts, batteries

Modeling Electron Transport

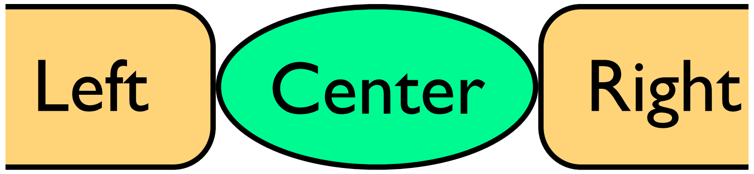
- Problem: Non-equilibrium
    - Driven system (applied bias)
- Assumption:
    - Steady-state quasi-equilibrium
    - Work in energy domain (Fourier transform)



Modeling Electron Transport



- Problem: System size
  - Intractably large for quantum mechanics
- Idea: Partition the system
  - Left (big)
  - Center (manageable?)
  - Right (big)



$$\hat{\mathcal{H}} \rightarrow \begin{bmatrix} \mathbf{H}_{\mathrm{LL}} & \mathbf{H}_{\mathrm{LC}} & \mathbf{0} \\ \mathbf{H}_{\mathrm{CL}} & \mathbf{H}_{\mathrm{CC}} & \mathbf{H}_{\mathrm{CR}} \\ \mathbf{0} & \mathbf{H}_{\mathrm{RC}} & \mathbf{H}_{\mathrm{RR}} \end{bmatrix}$$

Scattering Theory

Chemical Physics	Computational Mathematics
• Transport: Look at change in each partition's electron population • Only coherent (elastic) scattering • Zero temperature • Channels	• Try to formulate all quantities in terms of the central region • Rely on block tridiagonal matrix structure • $\Gamma G \Gamma G^\dagger$ is positive semi-definite

Open-system boundary conditions

$$I = \frac{2e}{h} \int_{E_\mathrm{F} - eV/2}^{E_\mathrm{F} + eV/2} \mathrm{d}E \, \underbrace{\mathrm{Tr}\left[\boldsymbol{\Gamma}_\mathrm{L}(E) \mathbf{G}_\mathrm{CC}(E) \boldsymbol{\Gamma}_\mathrm{R}(E) \mathbf{G}^\dagger_\mathrm{CC}(E)\right]}_{T(E)}$$

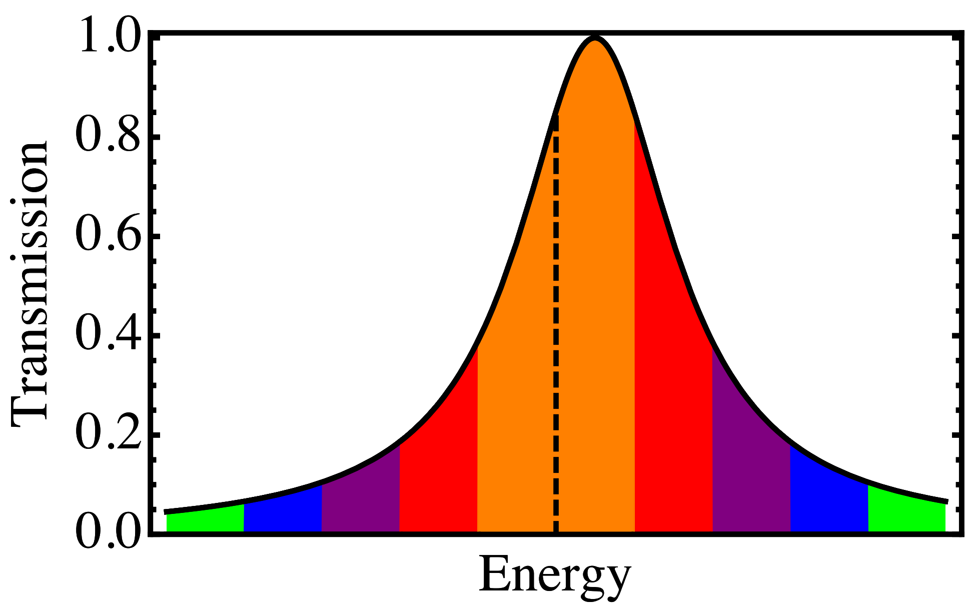
Correlation functions

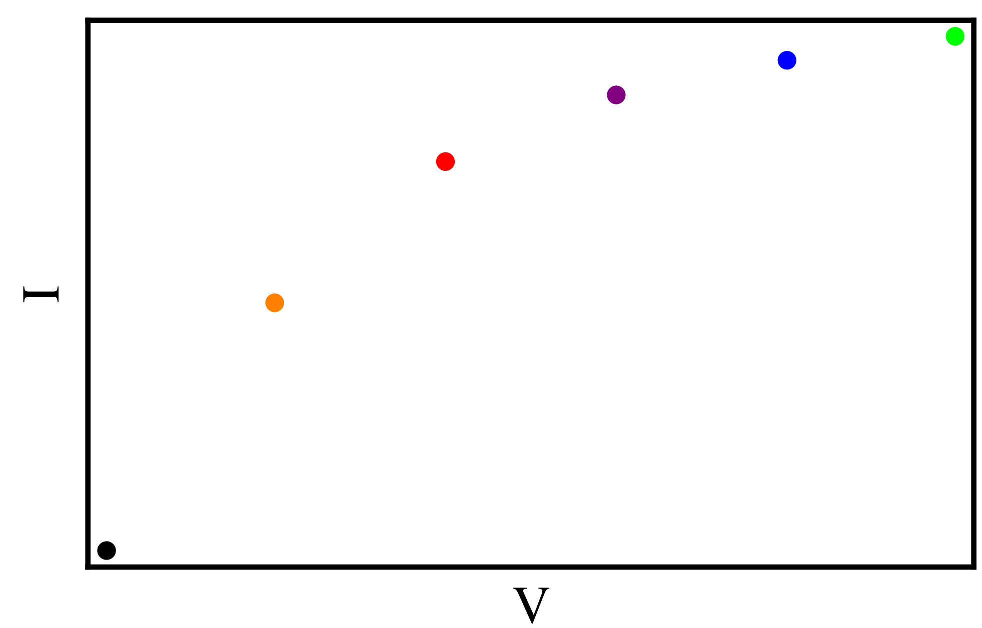
Imry & Landauer, Rev. Mod. Phys. **71**, S306 (1999).
Thygesen, Phys. Rev. B **73**, 035309 (2006).

Coherent Electron Transport

- "Conductance as transmission"
  - Conduction channels
  - Current saturation
- Theory/computation & experiment

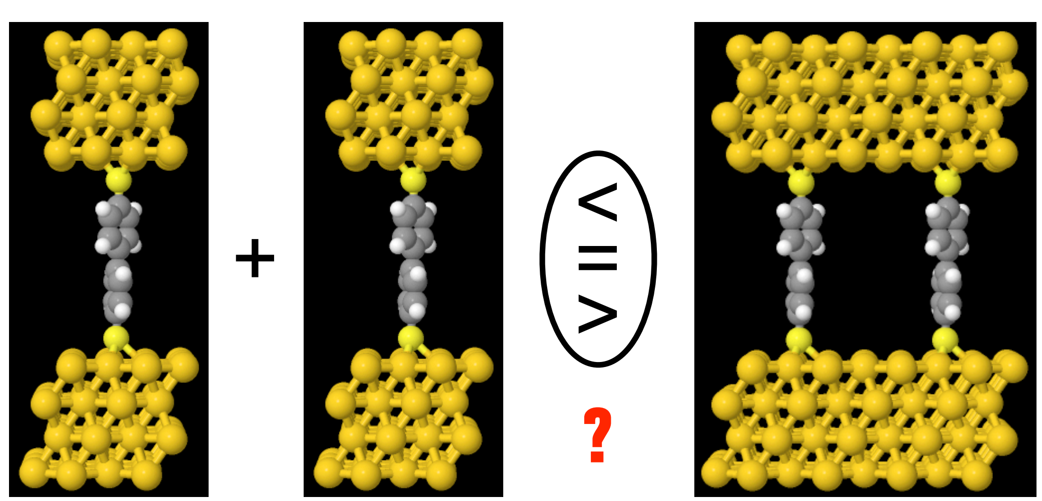
$$I = \frac{2e}{h} \int_{E_\mathrm{F}-eV/2}^{E_\mathrm{F}+eV/2} \mathrm{d}E\, T(E)$$

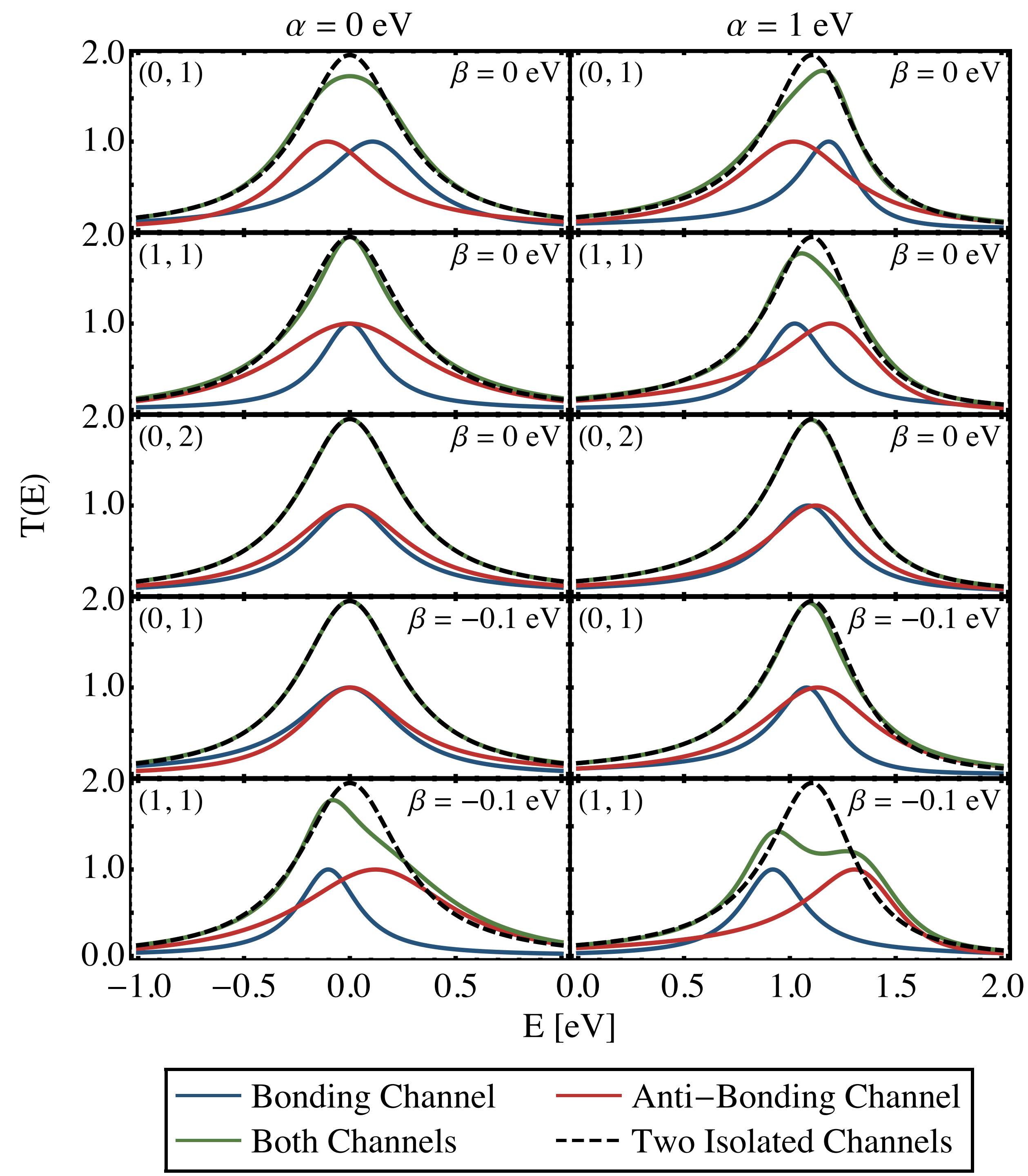




Quantum vs. Classical

- What if we have two channels?
    - Crosstalk
    - Eigenchannels
- Phase mismatches between channels

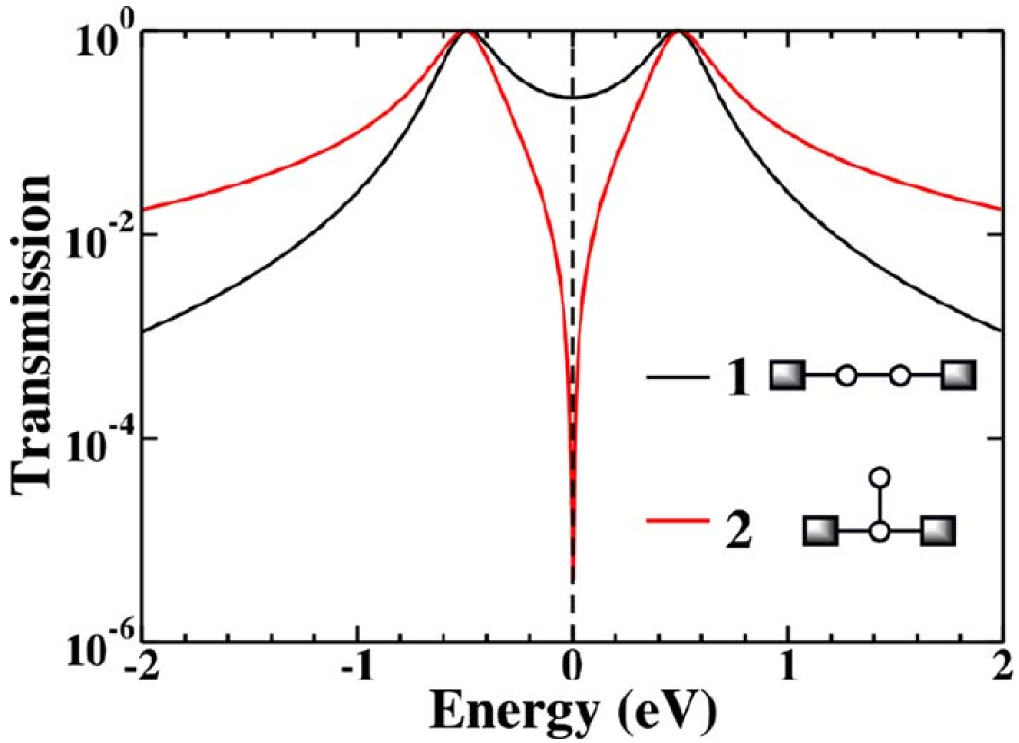




Reuter *et al.*, J. Phys. Chem. Lett. **2**, 1667 (2011).

Quantum Interference

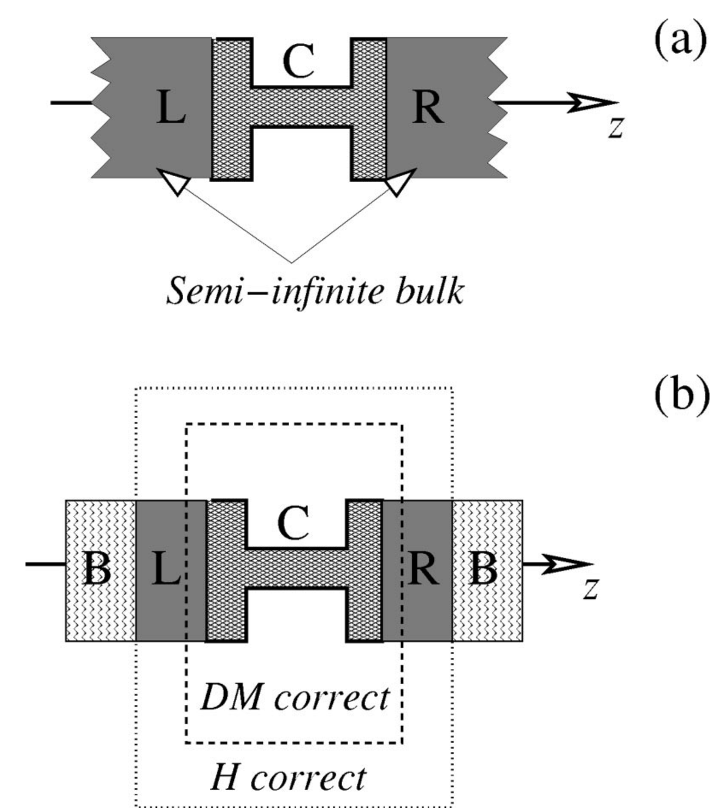
- Can we make the phases cancel each other?
  - Yes! Quantum interference
  - Zero transmission (perfect insulator)
- But this is from a toy model
  - Exercise in graph theory?
  - Real physical effect?



Solomon *et al.*, J. Chem. Phys. **129**, 054701 (2008).

Going Beyond Toy Models

- Use quantum chemistry codes to obtain Hamiltonian matrix
  - System partitioning
  - Maybe a little knitting involved
- These codes use (primarily) Gaussian basis sets
  - Non-orthogonal
  - Partitioning of basis functions



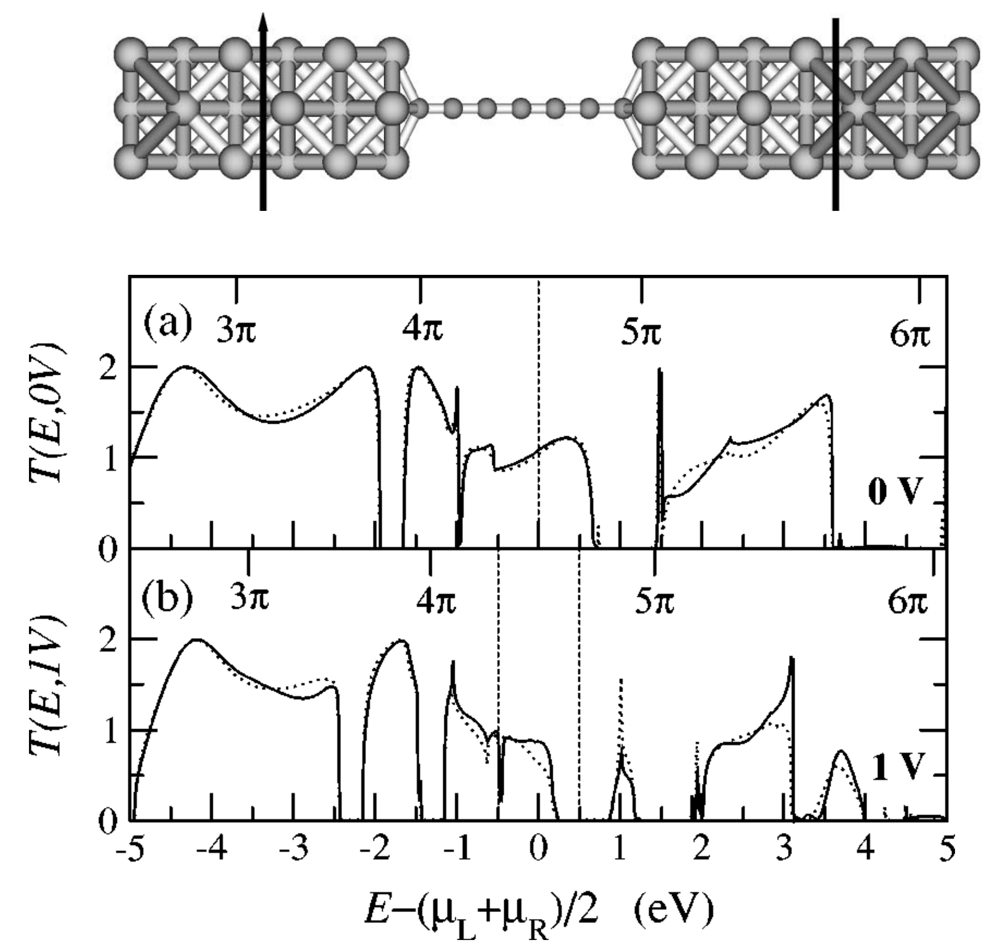
$$\begin{bmatrix} \mathbf{H}_{\mathrm{LL}} & \mathbf{H}_{\mathrm{LC}} & \mathbf{0} \\ \mathbf{H}_{\mathrm{CL}} & \mathbf{H}_{\mathrm{CC}} & \mathbf{H}_{\mathrm{CR}} \\ \mathbf{0} & \mathbf{H}_{\mathrm{RC}} & \mathbf{H}_{\mathrm{RR}} \end{bmatrix}$$

$$\begin{bmatrix} \mathbf{S}_{\mathrm{LL}} & \mathbf{S}_{\mathrm{LC}} & \mathbf{0} \\ \mathbf{S}_{\mathrm{CL}} & \mathbf{S}_{\mathrm{CC}} & \mathbf{S}_{\mathrm{CR}} \\ \mathbf{0} & \mathbf{S}_{\mathrm{RC}} & \mathbf{S}_{\mathrm{RR}} \end{bmatrix}$$

Brandbyge *et al.*, Phys. Rev. B **65**, 165401 (2002).

Going Beyond Toy Models (II)

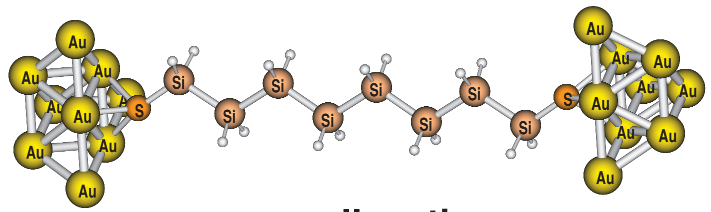
- Still "conductance as transmission"
  - Formula for $T(E)$ slightly more crunchy; no issues
  - Isolated vs. resonance states
- Basis set convergence
  - Bigger / better / "more complete" basis set should be used



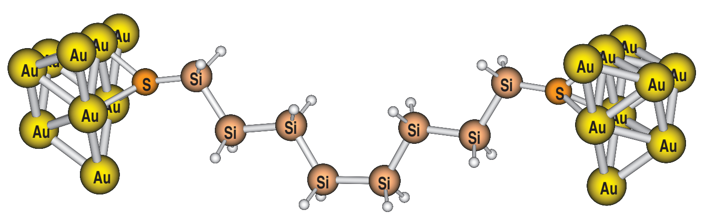
Brandbyge *et al.*, Phys. Rev. B **65**, 165401 (2002).

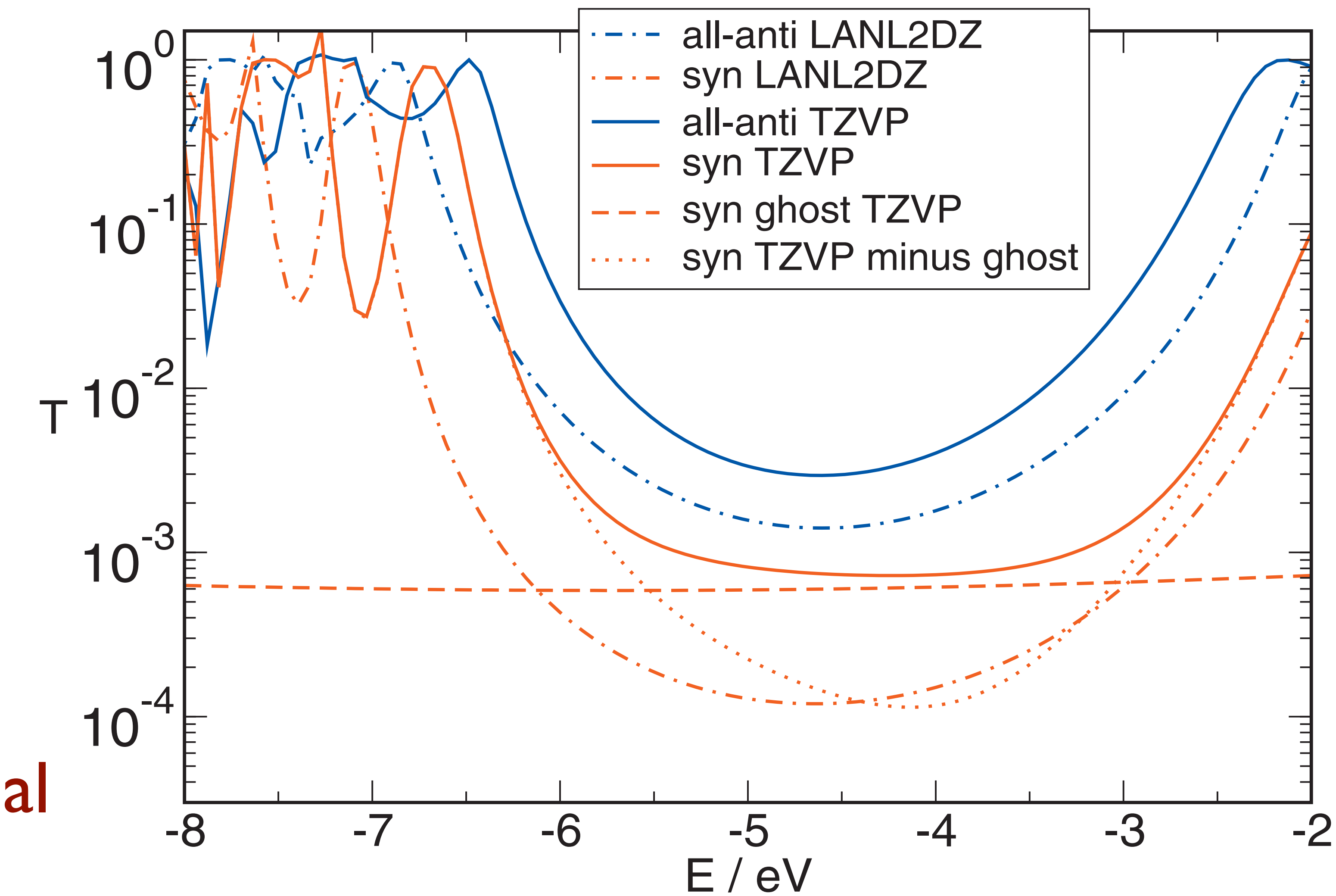
Thinking about Interference

No Interference



Interference





Bigger basis set defies chemical intuition!

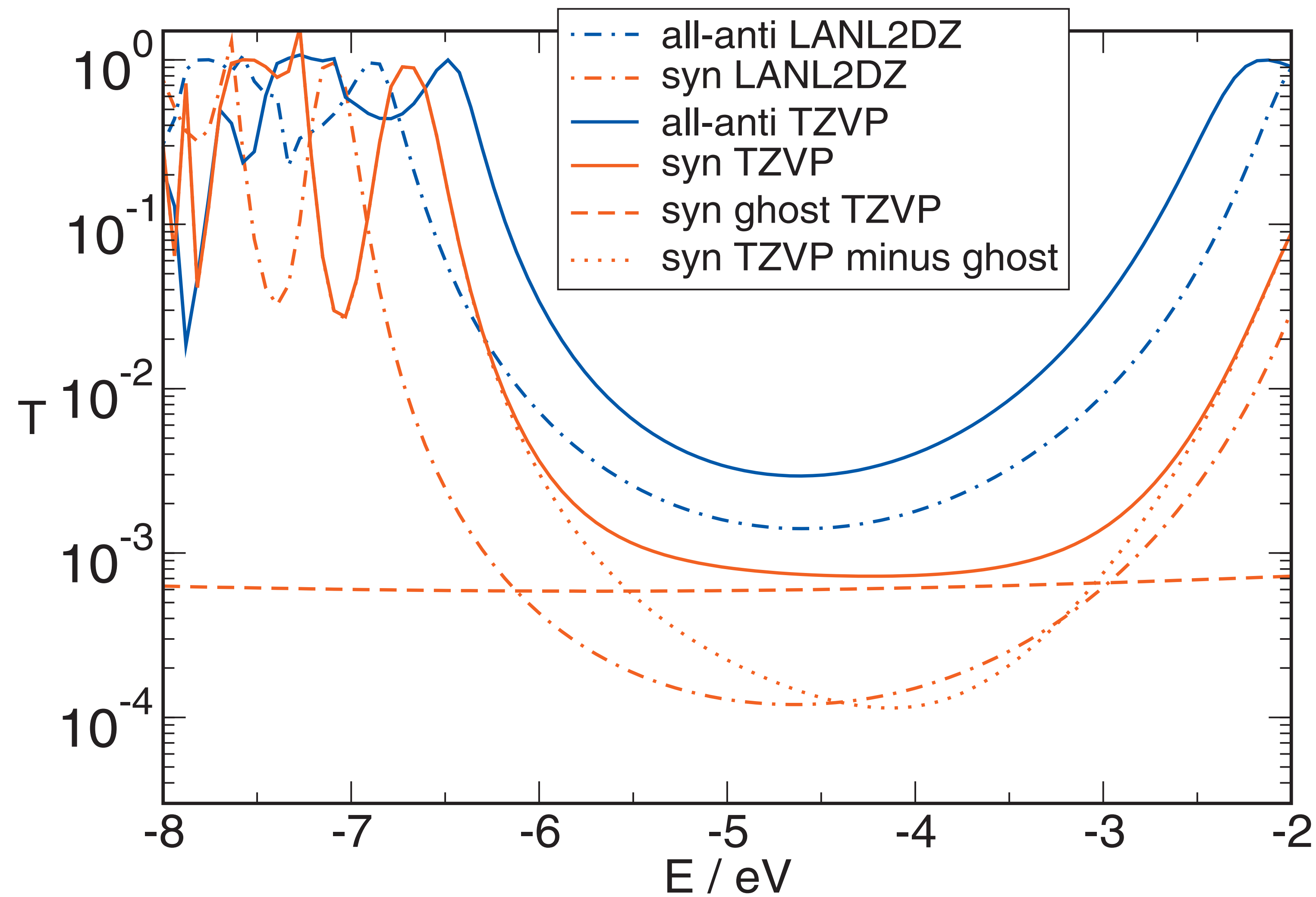
- Bug?
- System oddity?
- Model problem?

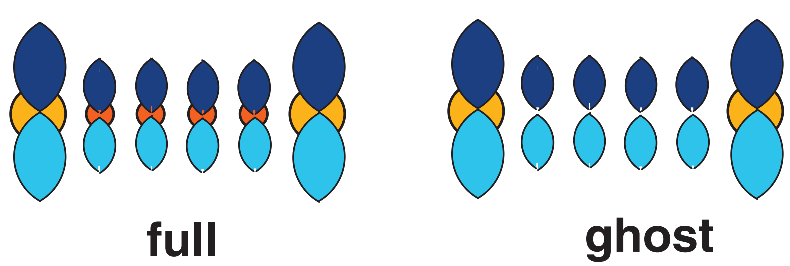
LANL2DZ = "Small" Basis Set
TZVP = "Big" Basis Set

Herrmann *et al.*, J. Chem. Phys. **132**, 024103 (2010).

The Importance of Validation

- Develop a test case
  - Vacuum tunneling
  - "Ghost" basis set
- Ghost transmission





LANL2DZ = "Small" Basis Set
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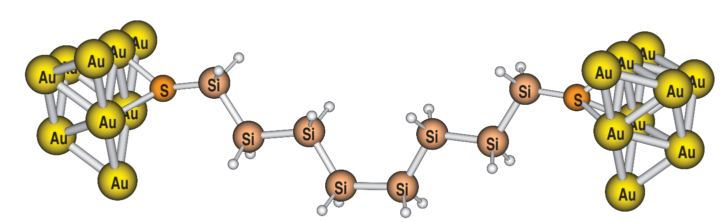

Herrmann *et al.*, J. Chem. Phys. **132**, 024103 (2010).

A Difficult Diagnosis

- System oddity?
- Hamiltonian?
- Overlap?
- Size of buffer region?
- Open-system boundary conditions?
  - System size, again

$$\begin{bmatrix} \mathbf{H}_{\mathrm{LL}} & \mathbf{H}_{\mathrm{LC}} & \mathbf{0} \\ \mathbf{H}_{\mathrm{CL}} & \mathbf{H}_{\mathrm{CC}} & \mathbf{H}_{\mathrm{CR}} \\ \mathbf{0} & \mathbf{H}_{\mathrm{RC}} & \mathbf{H}_{\mathrm{RR}} \end{bmatrix}$$

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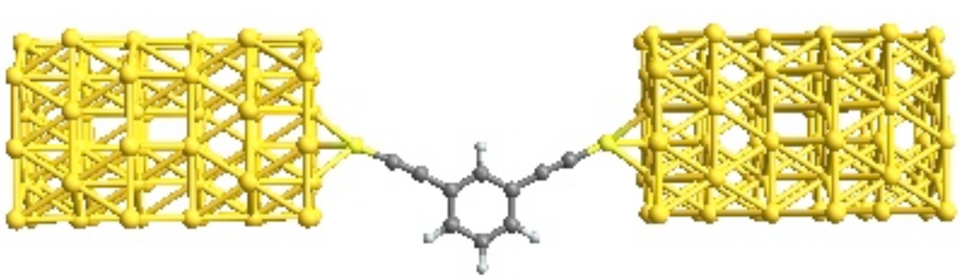
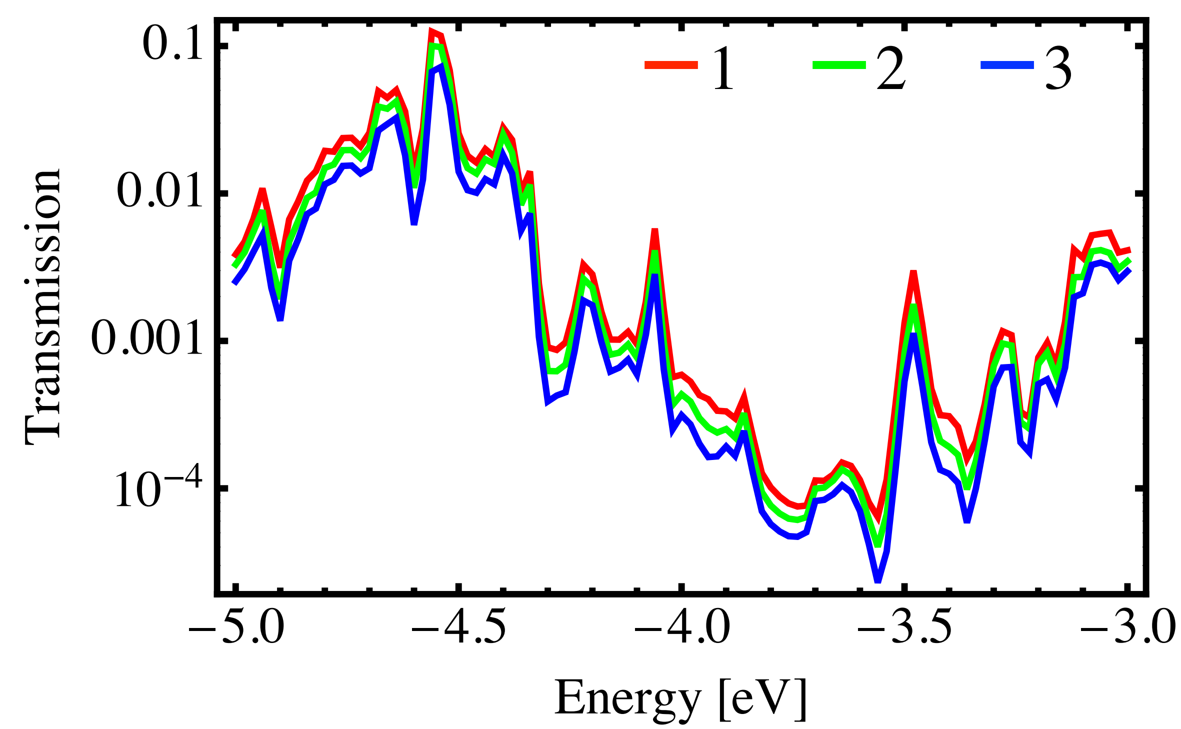


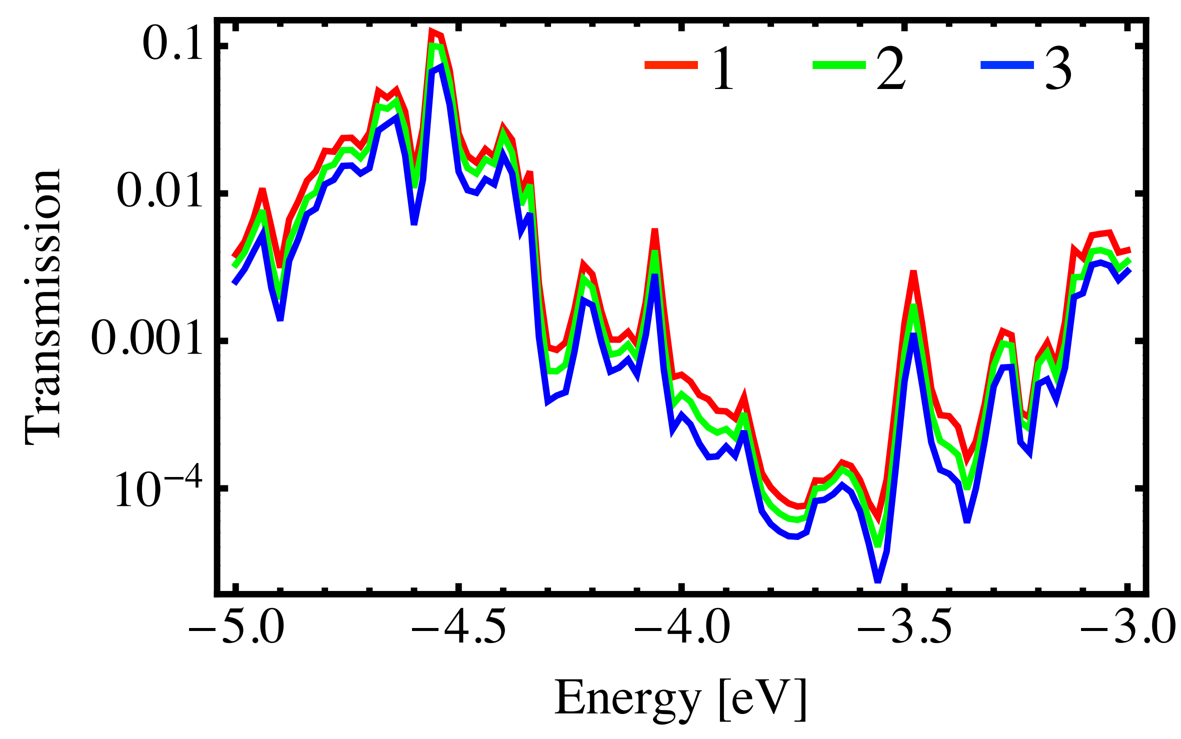


Herrmann *et al.*, J. Chem. Phys. **132**, 024103 (2010).

A Difficult Diagnosis (II)

- Revisiting assumptions
  - Physical
    - Coherent scattering
    - Zero temperature
  - Computational
    - Partitioning
    - Central region size

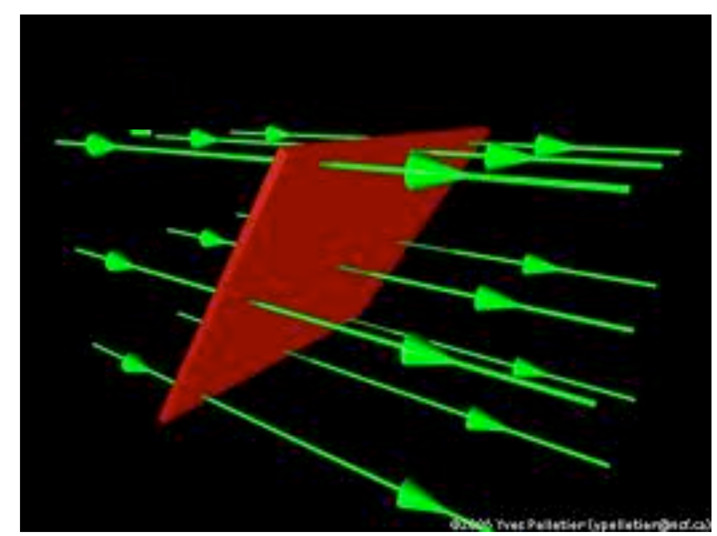
$$\begin{bmatrix} \mathbf{H}_{\mathrm{LL}} & \mathbf{H}_{\mathrm{LC}} & \mathbf{0} \\ \mathbf{H}_{\mathrm{CL}} & \mathbf{H}_{\mathrm{CC}} & \mathbf{H}_{\mathrm{CR}} \\ \mathbf{0} & \mathbf{H}_{\mathrm{RC}} & \mathbf{H}_{\mathrm{RR}} \end{bmatrix}$$



Computation vs. Physics

- Partitioning
  - Assign each basis function to one of the three regions
    - Easily implemented
  - What does the *operator* look like?
    - Non-orthogonal projector
  - May account for system size dependence

$$\begin{bmatrix} \mathbf{H}_{\mathrm{LL}} & \mathbf{H}_{\mathrm{LC}} & \mathbf{0} \\ \mathbf{H}_{\mathrm{CL}} & \mathbf{H}_{\mathrm{CC}} & \mathbf{H}_{\mathrm{CR}} \\ \mathbf{0} & \mathbf{H}_{\mathrm{RC}} & \mathbf{H}_{\mathrm{RR}} \end{bmatrix}$$



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

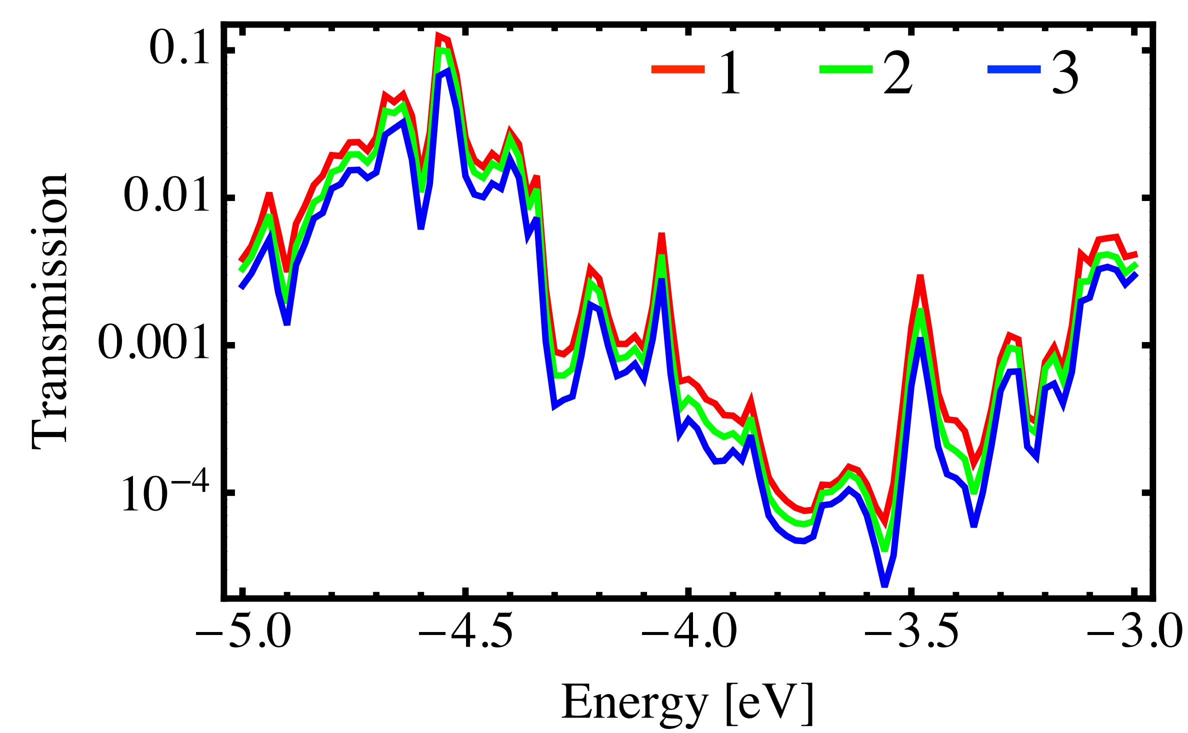
Matrices vs. Operators

- Central region size
  - Corner blocks of $\mathbf{H}, \mathbf{S}$ are $\mathbf{0}$
- Matrix block?
  - *Operator*
  - Perhaps we meant to say

$$\hat{\mathcal{N}}_{\mathrm{L}}\, \hat{\mathcal{H}}\, \hat{\mathcal{N}}_{\mathrm{R}}^{\dagger} = \hat{0}$$

$$\begin{bmatrix} \mathbf{H}_{\mathrm{LL}} & \mathbf{H}_{\mathrm{LC}} & \mathbf{0} \\ \mathbf{H}_{\mathrm{CL}} & \mathbf{H}_{\mathrm{CC}} & \mathbf{H}_{\mathrm{CR}} \\ \mathbf{0} & \mathbf{H}_{\mathrm{RC}} & \mathbf{H}_{\mathrm{RR}} \end{bmatrix}$$

Size	Norm [keV]
1	1.0
2	11.7
3	0.4

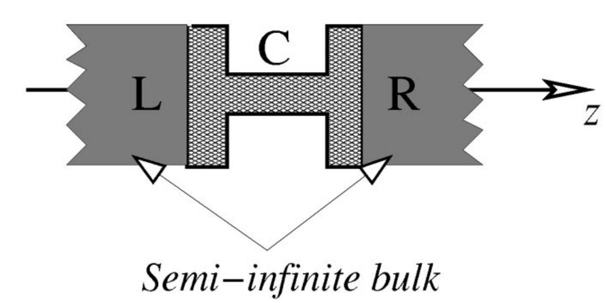


Ghost transmission is a numerical short-circuit!

Using Projection Operators

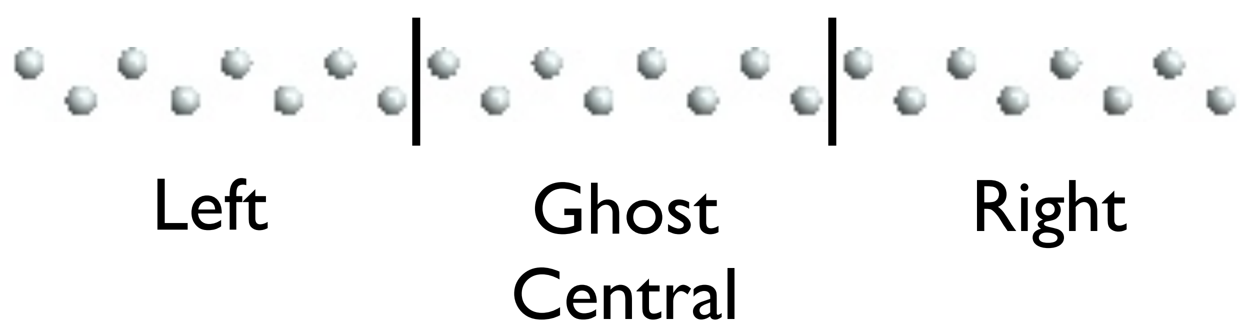
- Derivation of current formula proceeds similarly
  - Use zero *projection* instead of zero matrix block
- Result is computationally more expensive; requires $\mathbf{S}^{-1}$
- Good opportunity to redefine projectors (orthogonal)
  - Not defined by the basis set; defined by physics
  - Should remove basis set dependence (assume completeness)
  - Requires more than standard codes output

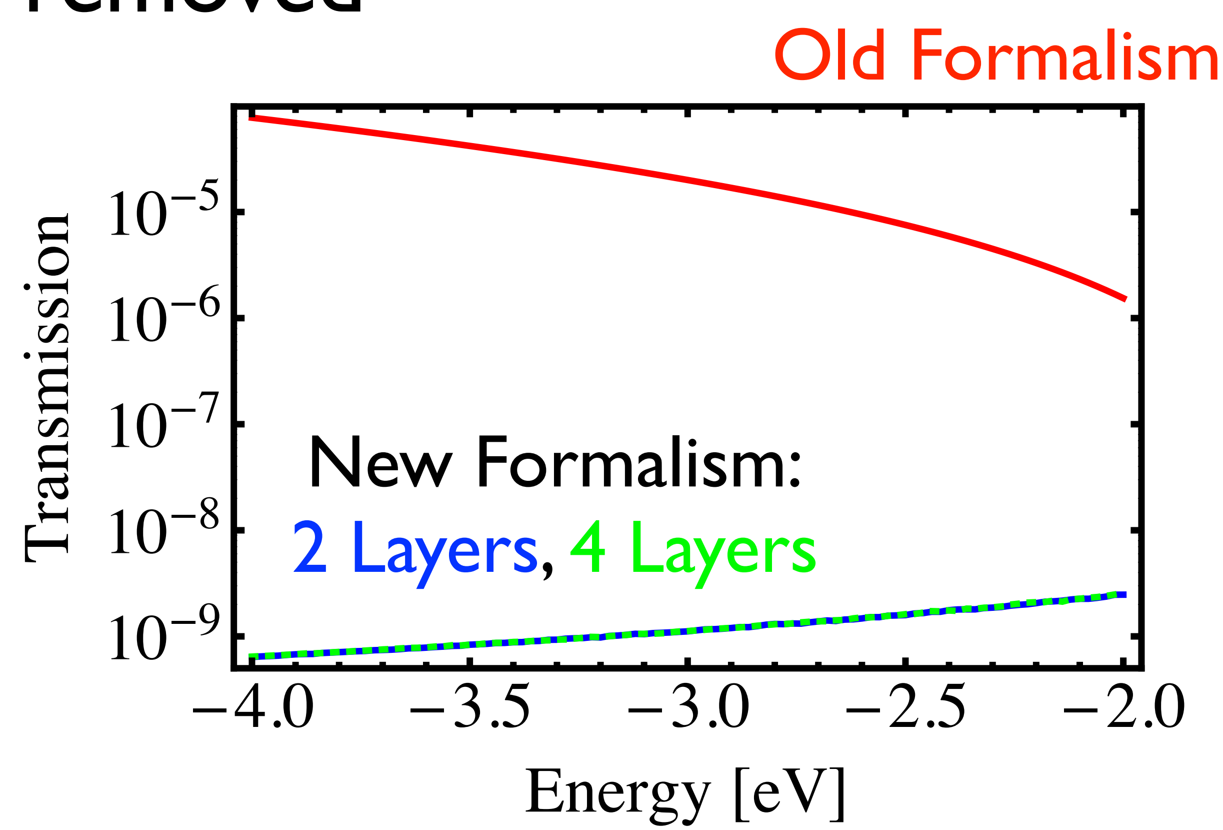
$$\int_{z_-}^{z_+} \mathrm{d}z \int_{-\infty}^{\infty} \mathrm{d}y \int_{-\infty}^{\infty} \mathrm{d}x \varphi_j(\mathbf{x})^* \varphi_k(\mathbf{x})$$



Validation

- Simple, model system
  - Chain of hydrogen atoms
- New transmissions are considerably smaller
  - More in line with expected results
  - System size dependence is removed





Summary

- Diagnosed ghost transmission in electron transport calculations
- Discovered the importance of unit testing
  - Codes, test systems, models
  - Don't lose sight of the application when doing computation!
  - Get the right answer for the right reasons

Future Directions

- Correlate chemistry with electron transport properties
- Conductance pathways
  - Disordered systems
- Reconciling experiment & computation
  - Bridge the transmission function and the current

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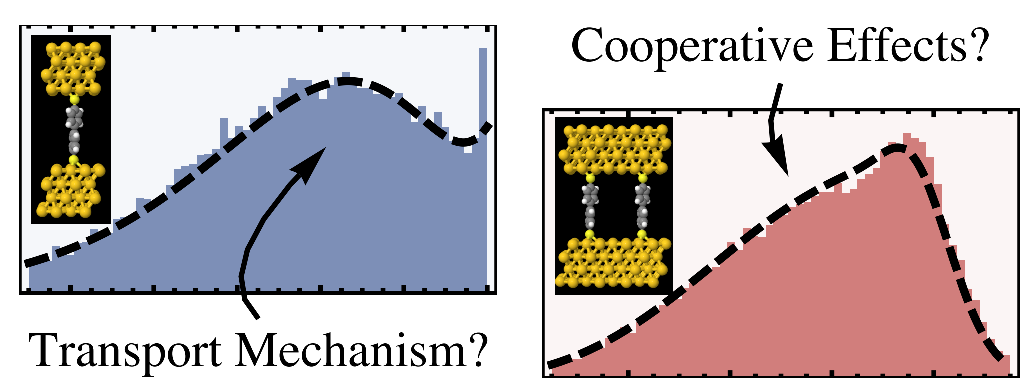

With Many Thanks

- Robert Harrison
- Bobby Sumpter
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- OLCF (this work used Jaguar)
- Krell Institute & DOE CSGF