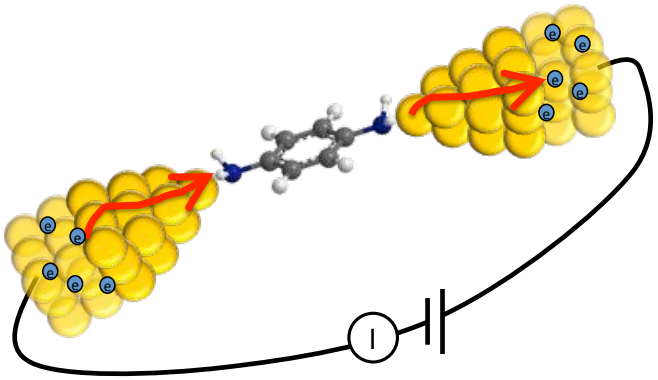
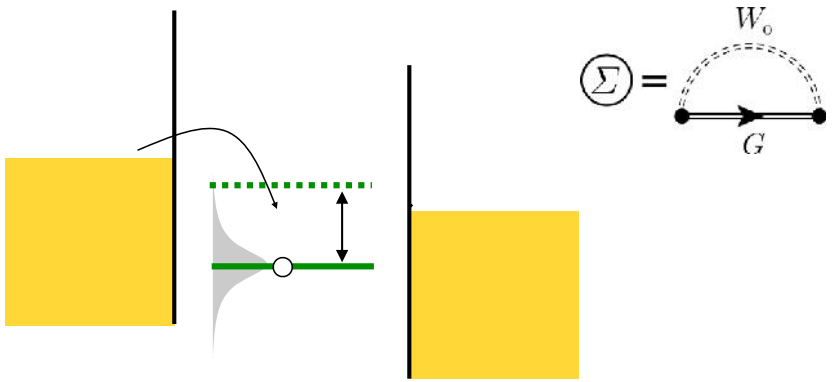
Charge Transport and Energy Level Alignment with Ab Initio Methods





$$T(E) = \mathrm{Tr}\left[\Gamma_{\mathrm{L}} G'^{\dagger}_{\mathrm{C}} \Gamma_{\mathrm{R}} G'_{\mathrm{C}}\right]$$

Jeffrey B. Neaton

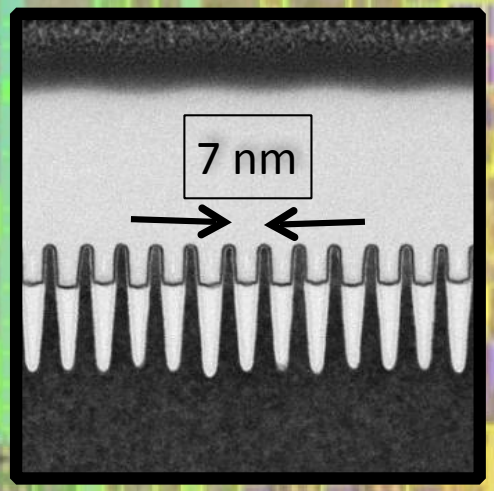
Department of Physics, University of California, Berkeley
Molecular Foundry, Lawrence Berkeley National Laboratory
Kavli Institute for Energy Nanosciences at Berkeley

Cal BERKELEY LAB SciDAC Scientific Discovery through Advanced Computing MOLECULAR FOUNDRY

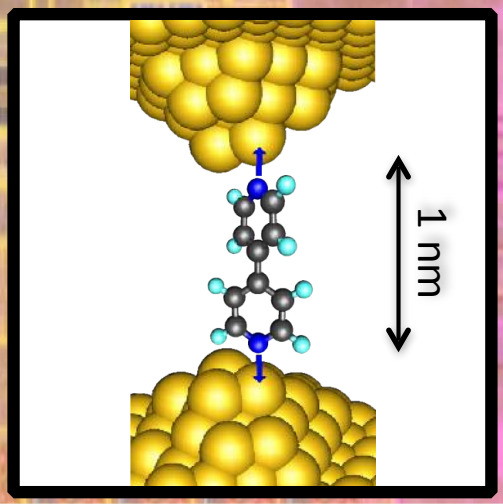
Progression of Circuitry to the Molecular Scale

Explore electronic circuit components with molecular building blocks at unchartered length scale close to fundamental limit

Intel core i7 2010



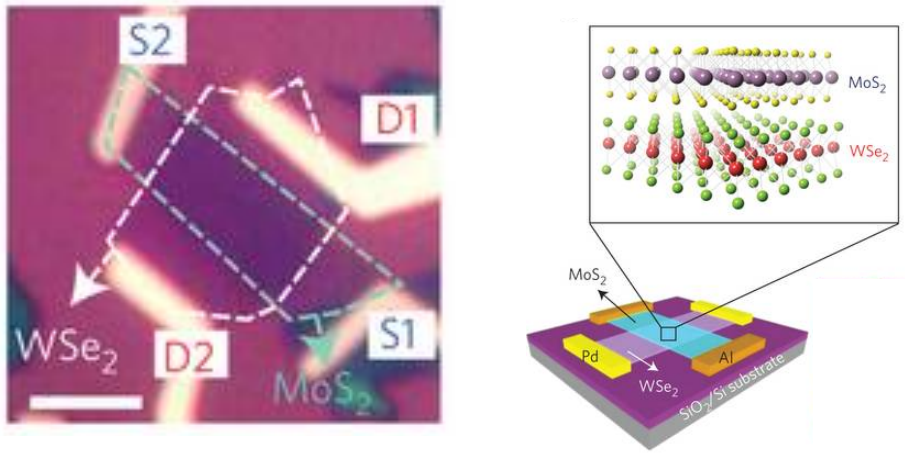
Transistor, IBM 2015



Molecular switch, 2009

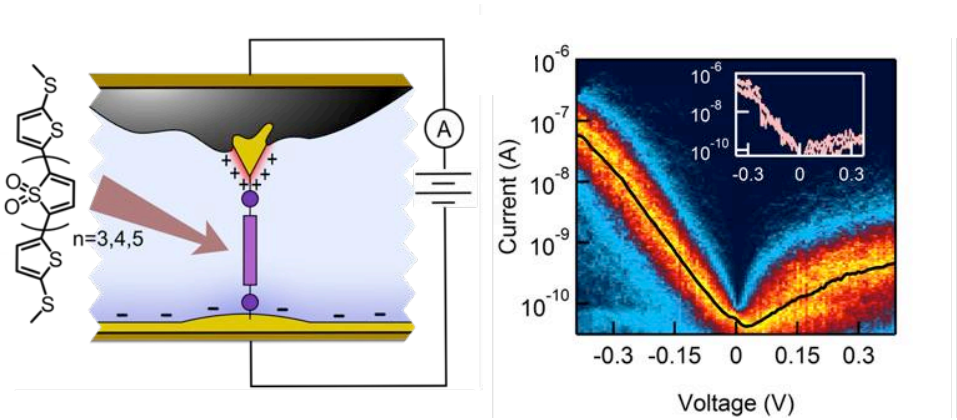
Examples of Hybrid Interfaces in Nanoscale Devices

2D van der Waals Heterojunctions



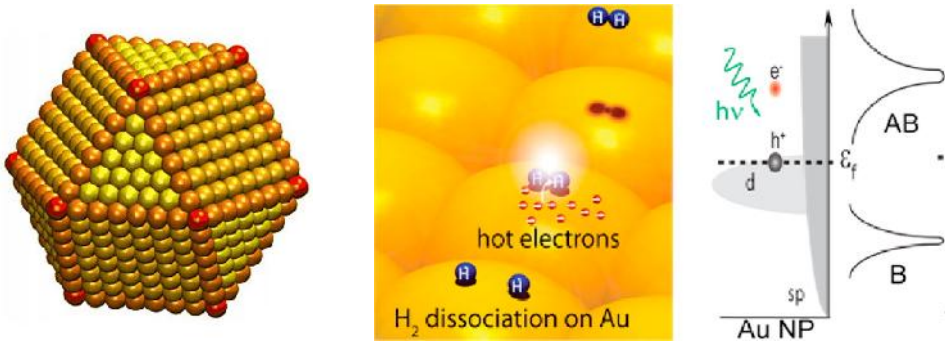
Kim, Hone, Heinz et al, Nature Nano. (2014)

Single-Molecule Junctions



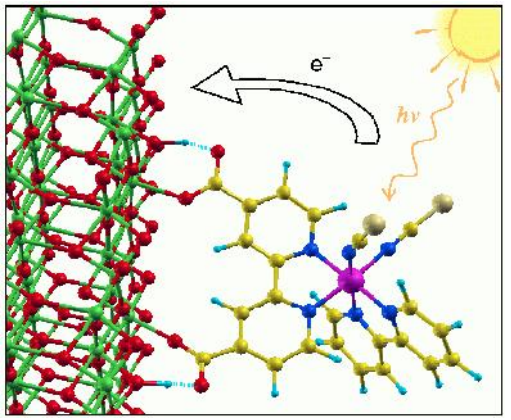
Venkataraman, Campos, Neaton, et al, Nature Nano. (2015)

Photocatalysis with Nanoparticles

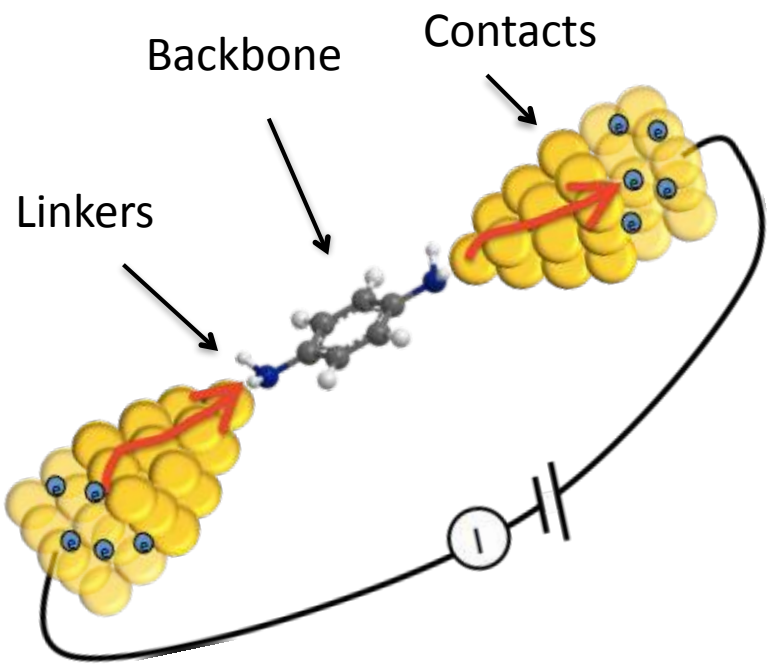


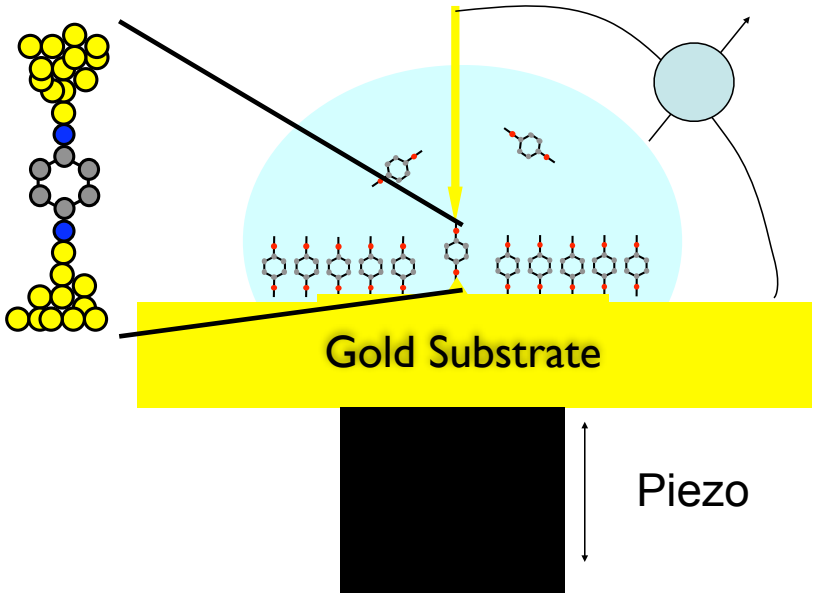
Halas et al, Nano Lett. **13**, 240 (2013)

Dye-Sensitized Solar Cells



Single-Molecule Conductance Measurements: STM-Break Junctions w/ Statistics



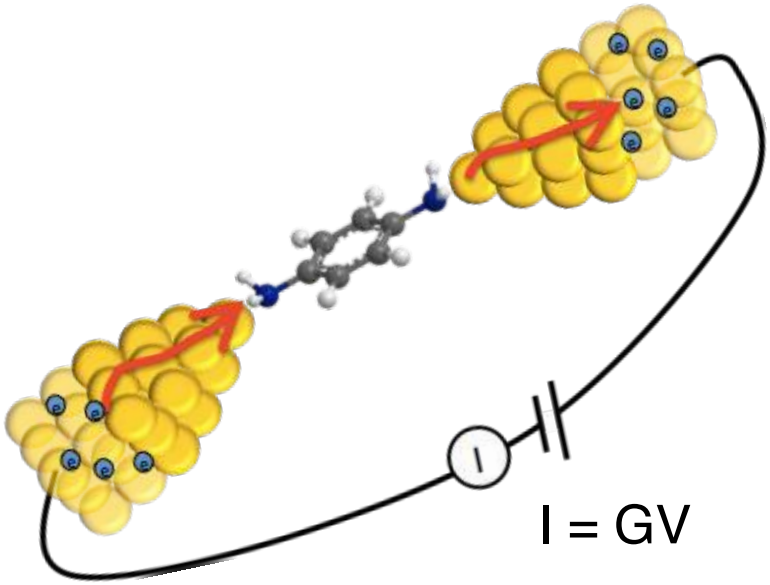


Xu and Tao, Science **301**, 1221 (2003)

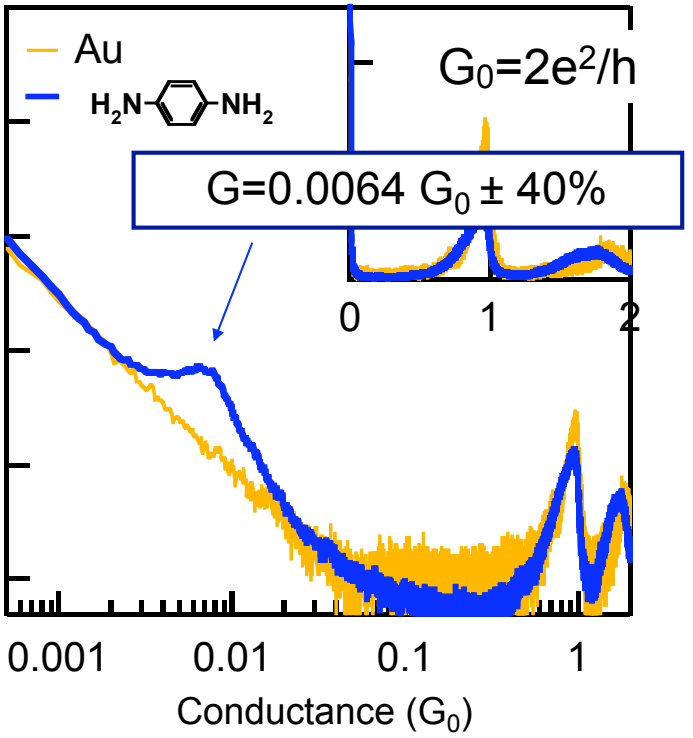
Venkataraman, Hybertsen *et al*, Nature **442**, 904 (2006)

See also e.g. van de Zant, Agrait, Natelson, Scheer, Reddy, Tal, van Ruitenbeek, van der Molen…

Single-Molecule Conductance Measurements: STM-Break Junctions w/ Statistics

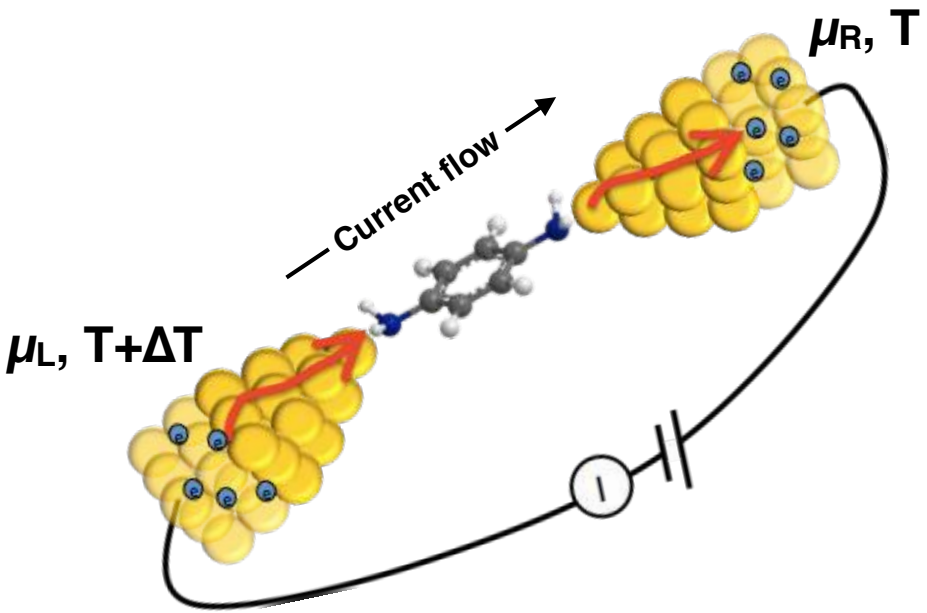


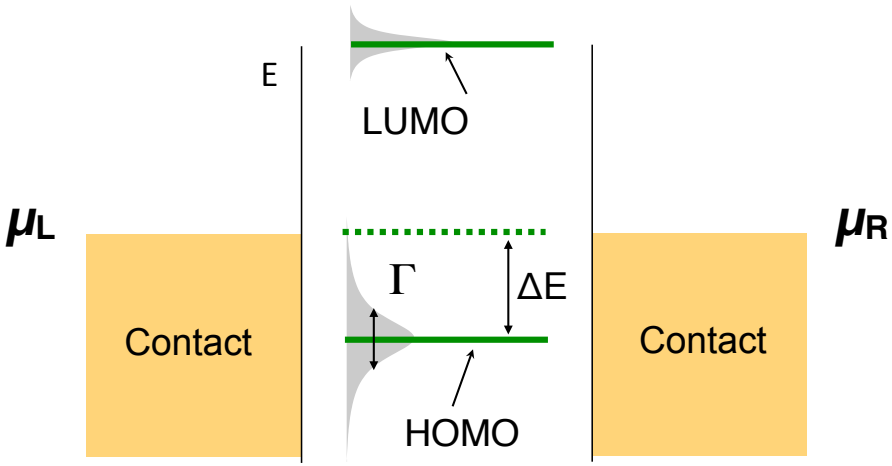
Au-benzene-diamine-Au



Venkataraman, Hybertsen *et al*,
Nature **442**, 904 (2006)

Charge Transport in Molecular Junctions

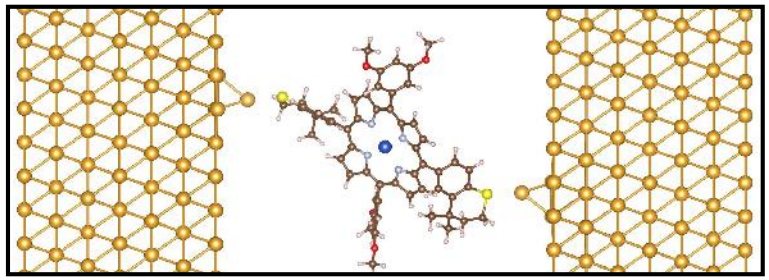




- Transport dominated by coherent tunneling
- Junction geometry, level alignment are central

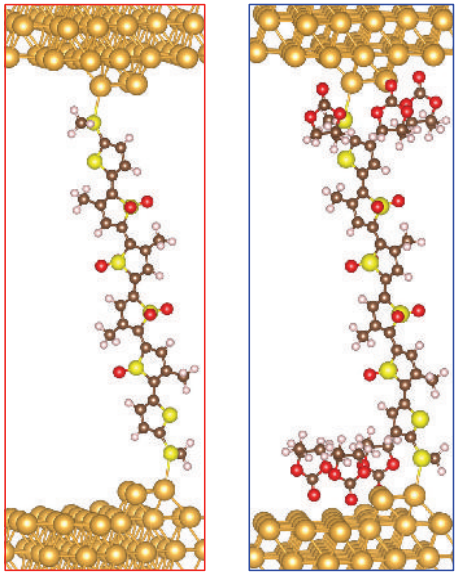
First Principles Approach

- **Density Functional Theory (DFT)**
  - Structural energetics
  - van der Waals dispersion
  - Hybrid functionals



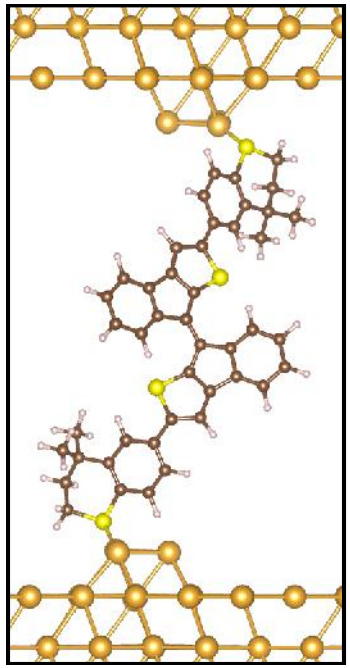
Liu, Neaton et al., Nano Lett. (2014)

1019 atoms

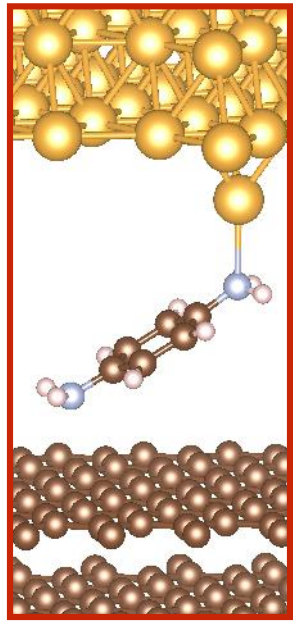


437 atoms

Capozzi, Liu, Neaton, Venkataraman et al., Nature Nano. (2015)



594 atoms



150 atoms

Kim, Liu, Neaton, Venkataraman et al PNAS (2014)

First Principles Approach

- **Density Functional Theory (DFT)**
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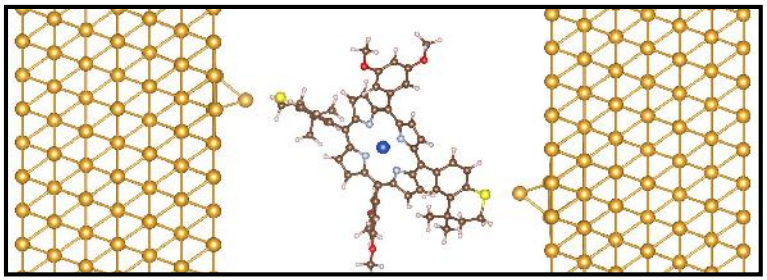
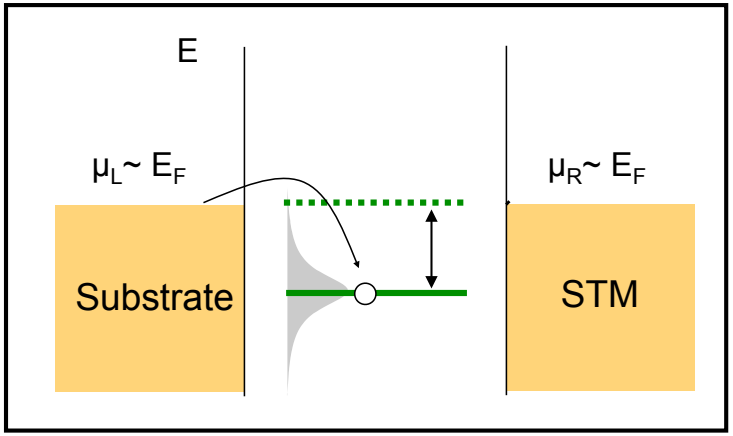
  - Hybrid functionals



Donor-acceptor linkers: -NH_2, -N, -alkyl sulfide, etc



First Principles Approach

- **Density Functional Theory (DFT)**
  - Structural energetics
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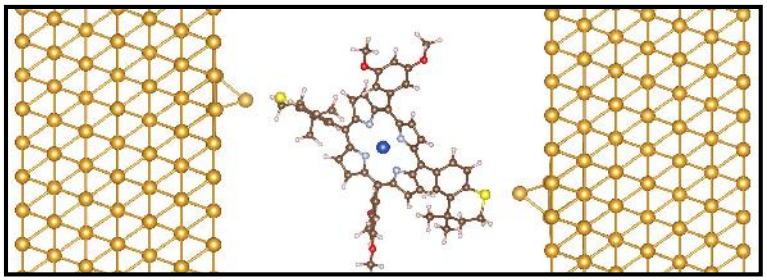
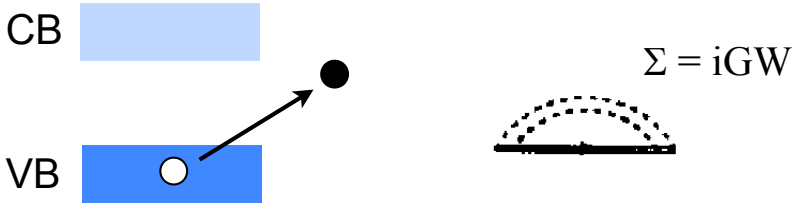
  - Hybrid functionals

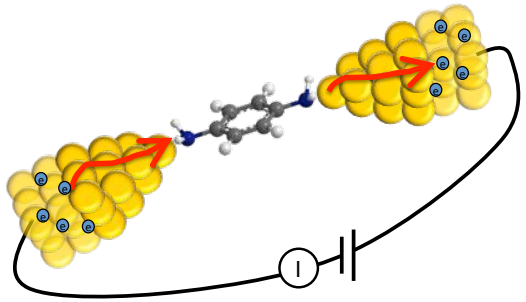


Donor-acceptor linkers: -NH_2, -N, -alkyl sulfide, etc

- **Many-Body Perturbation Theory (MBPT)**
  - GW approximation
    - Electron addition/removal, photoemission, transport

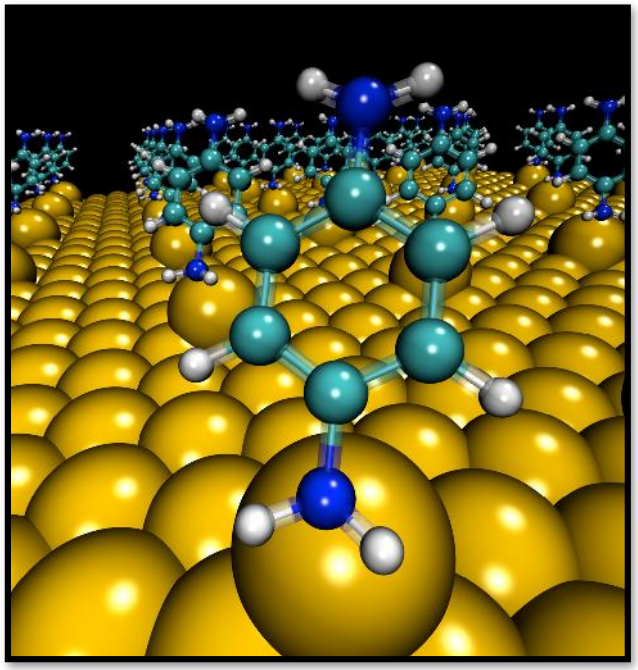


- **Non-Equilibrium Green's Functions (NEGF)**
  - *ab initio* conductance, thermopower, IV
  - approximate GW corrections

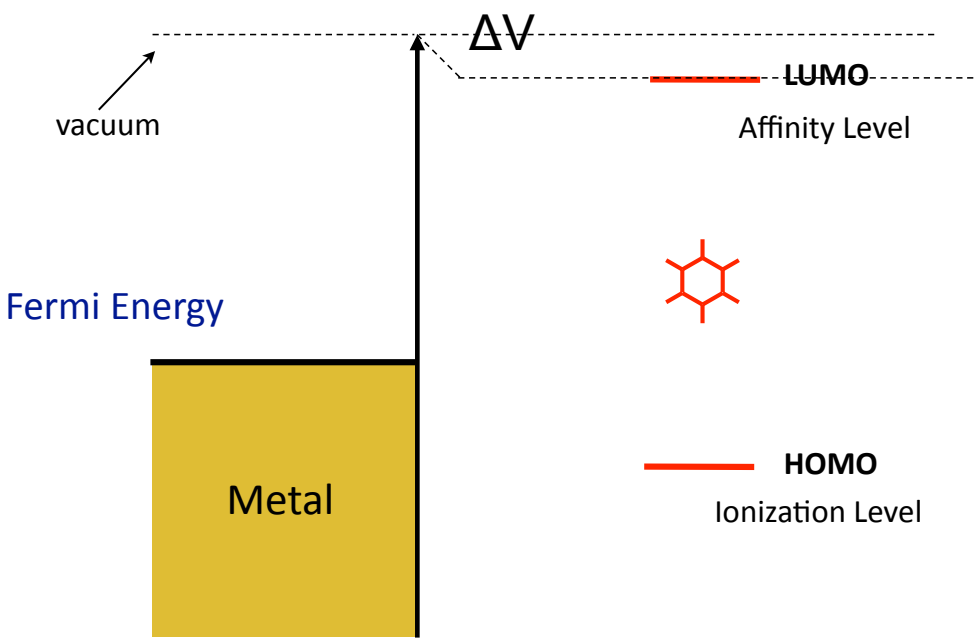


Level alignment at metal-molecule interfaces

Metal-molecule contact



Energy level diagram

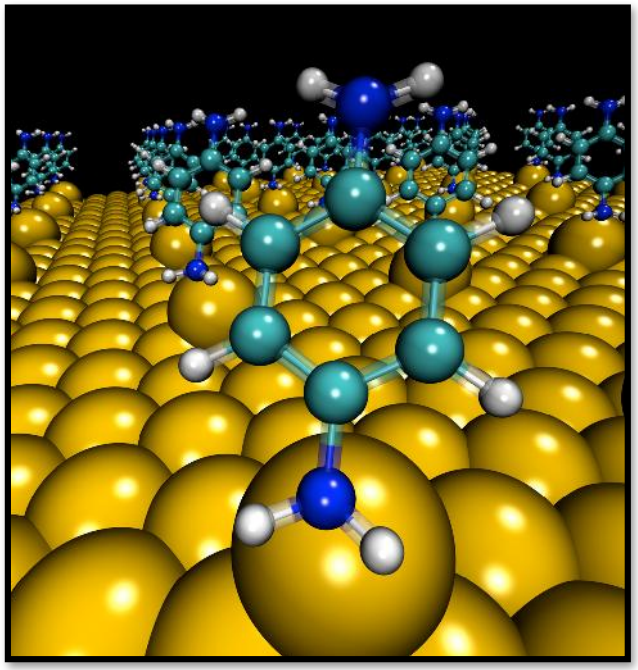


Physical effects influencing level alignment

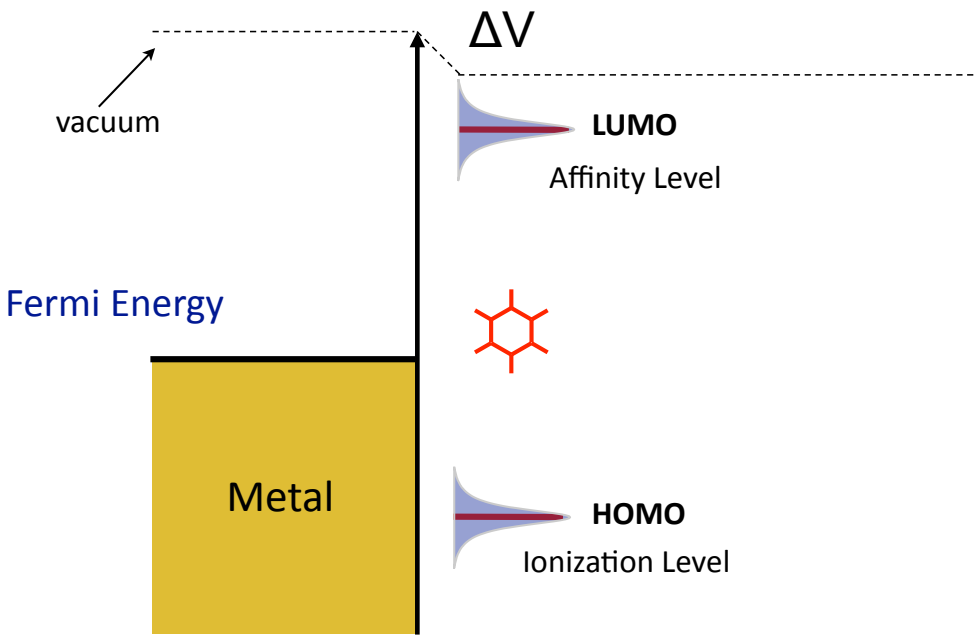
- Electronic structure of isolated systems: IP,EA and work function
- Charge rearrangement upon binding: Interface dipole

Level alignment at metal-molecule interfaces

Metal-molecule contact



Energy level diagram



Physical effects influencing level alignment

- Electronic structure of isolated systems: IP,EA and work function
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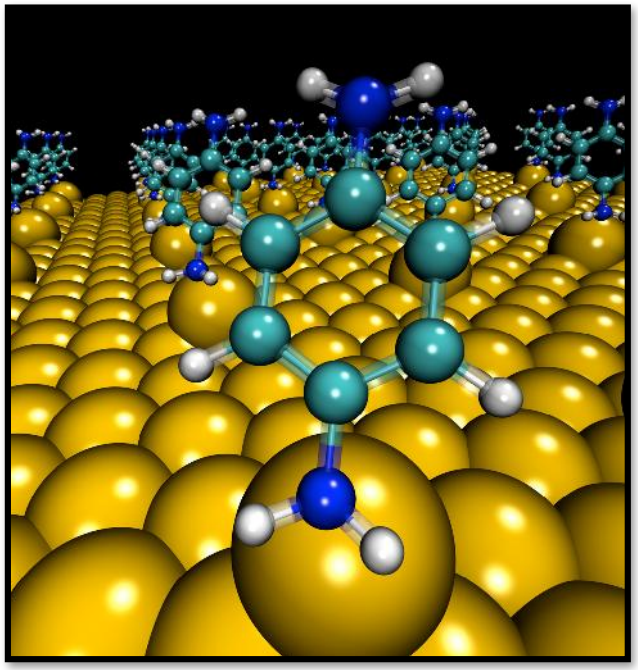
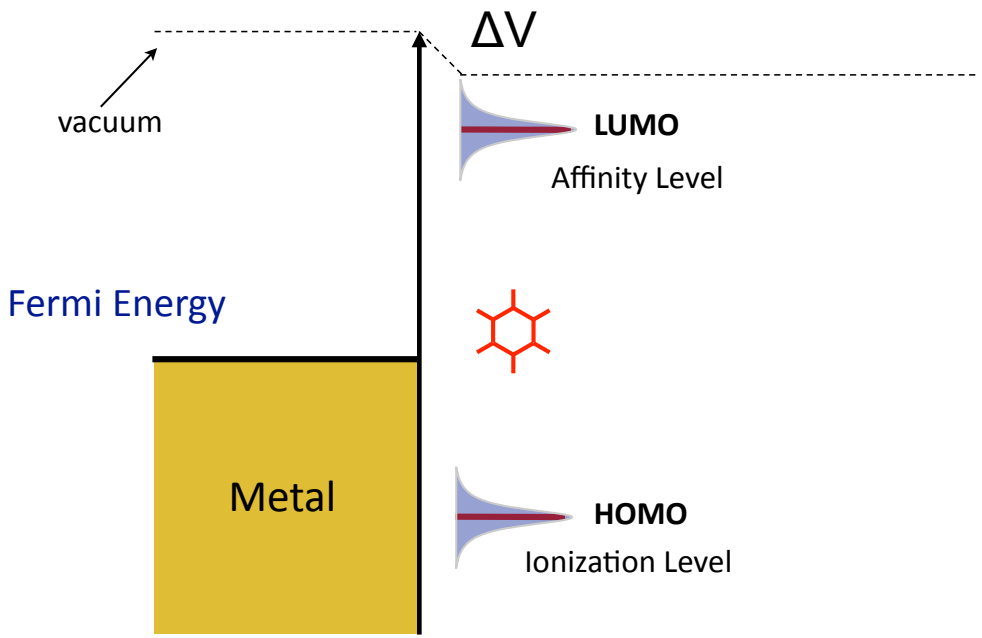
- Energy level broadening: Hybridization, lifetime

Level alignment at metal-molecule interfaces

Metal-molecule contact



Energy level diagram



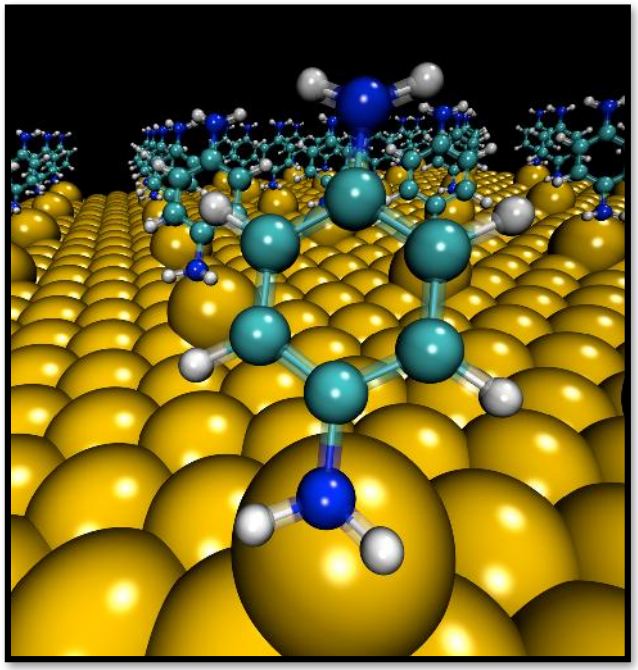
Physical effects influencing level alignment

- Electronic structure of isolated systems: IP,EA and work function
- Charge rearrangement upon binding: Interface dipole
- Energy level broadening: Hybridization, lifetime
- Electrode polarization: Non-local correlation

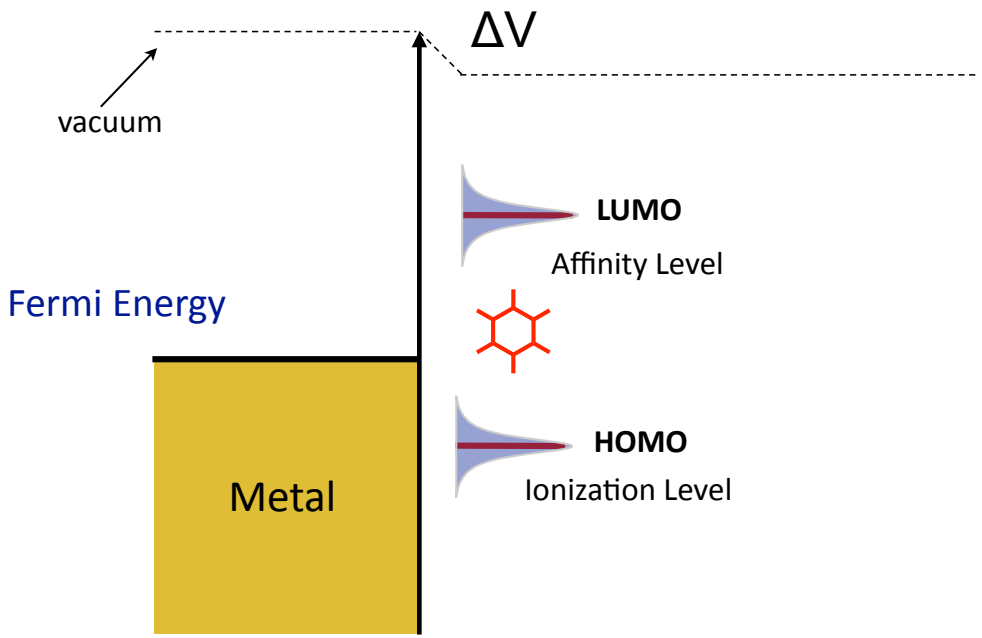
Kohn-Sham system from standard functionals inadequate.

Level alignment at metal-molecule interfaces

Metal-molecule contact



Energy level diagram

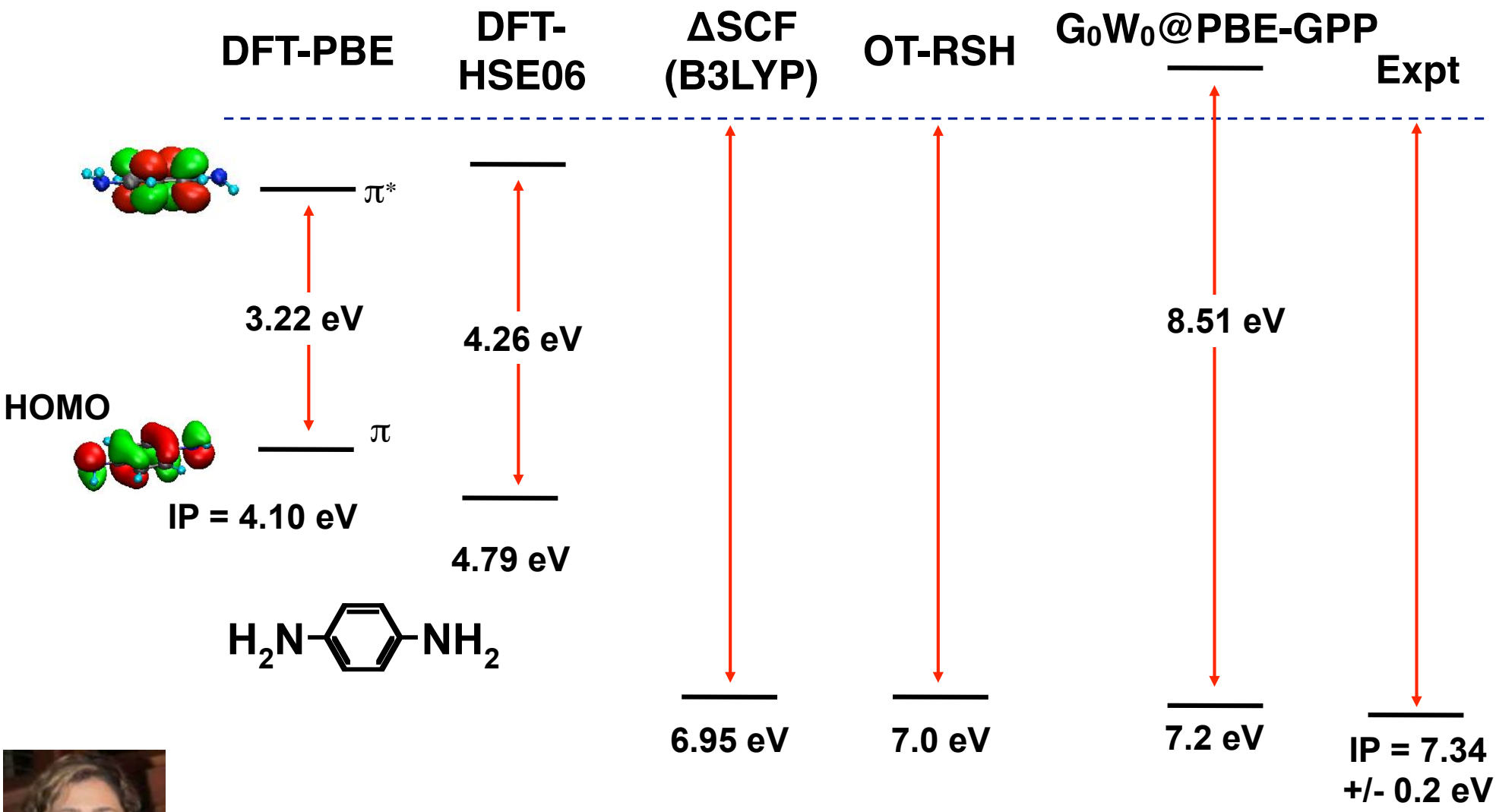


Physical effects influencing level alignment

- Electronic structure of isolated systems: IP,EA and work function
- Charge rearrangement upon binding: Interface dipole
- Energy level broadening: Hybridization, lifetime
- Electrode polarization: Non-local correlation

Generalized Kohn-Sham system from hybrid functionals is quite promising (see later in the talk)

Gas-Phase BDA Electron Removal Energies with GW



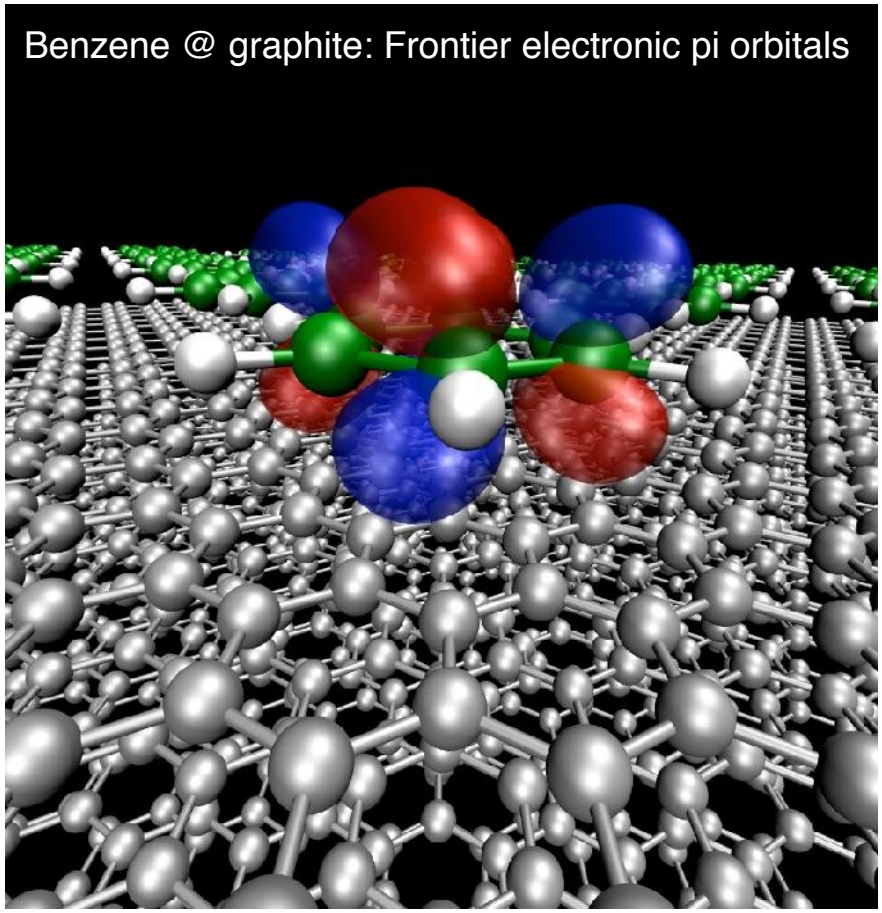
GW100 Rinke, Evers, Neaton et al, JCTC (2015)

G_0W_0@PBE-GPP MAE = 0.28 eV

G_0W_0@PBE-FF MAE = 0.71 eV

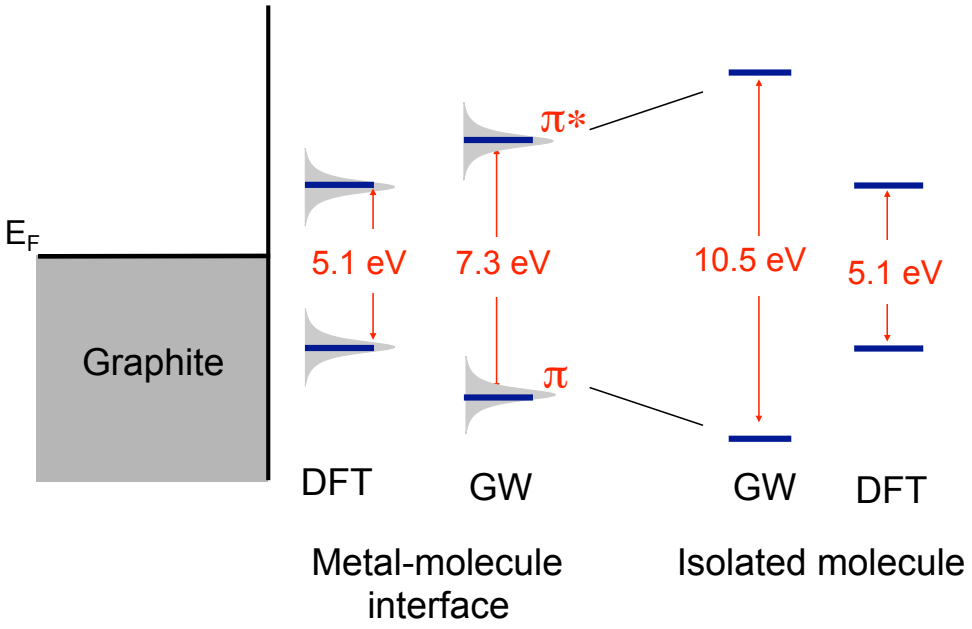
Sharifzadeh, Tamblyn, Doak, Darancet, Neaton, Europhys. J. B **85**, 323 (2012)

Molecular Levels Strongly Renormalized in Junction



Neaton, Hybertsen, Louie,
Phys. Rev. Lett. **97**, 216405 (2006)

Benzene @ graphite: Computed Level Diagram



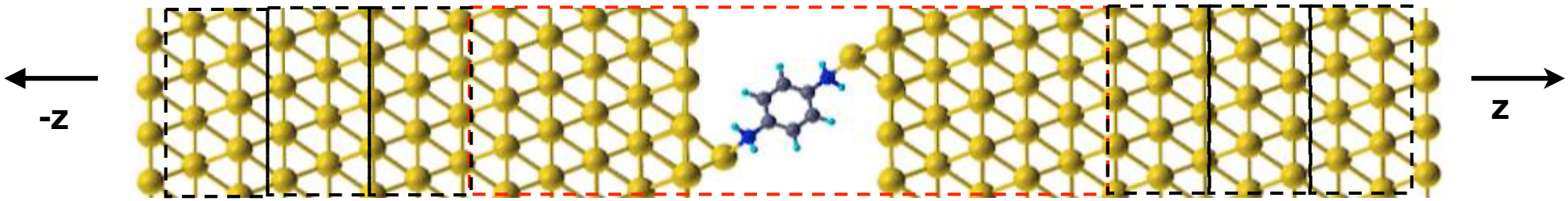
- Nonlocal electronic correlations, not present in DFT, between the molecule and substrate reduce gap

- Effect approximately captured by classical electrostatics

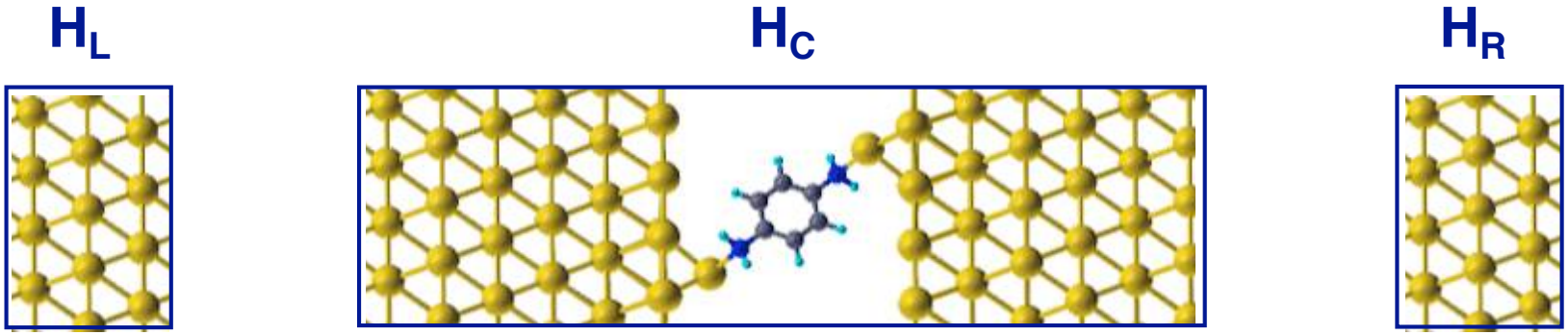
Corroborated by Thygesen, Rubio, Rinke, Sanvito

Steady-State Charge Transport with Open Boundary Conditions

Recast Hamiltonian **H** of the infinite open system…



…as three connected, tractable systems

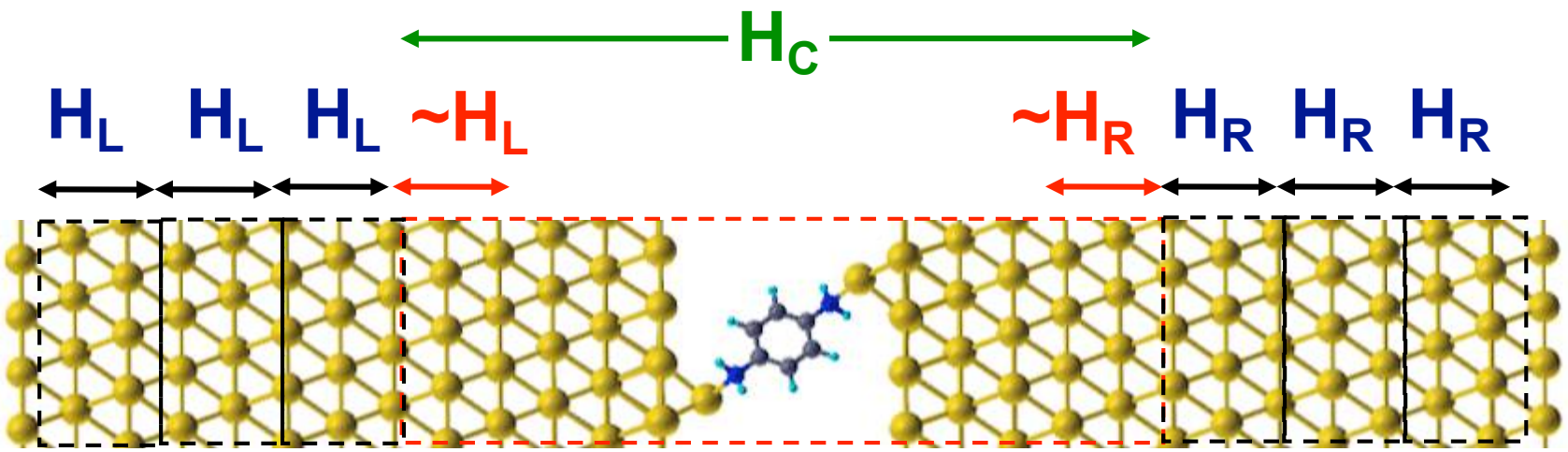


Left lead
(infinite but periodic)

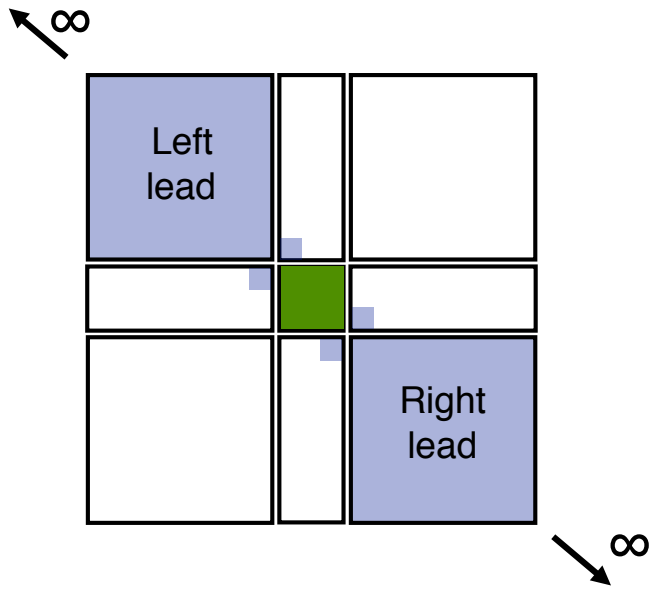
Conducting region
(finite)

Right lead
(infinite but periodic)

Hamiltonian matrix of infinite system



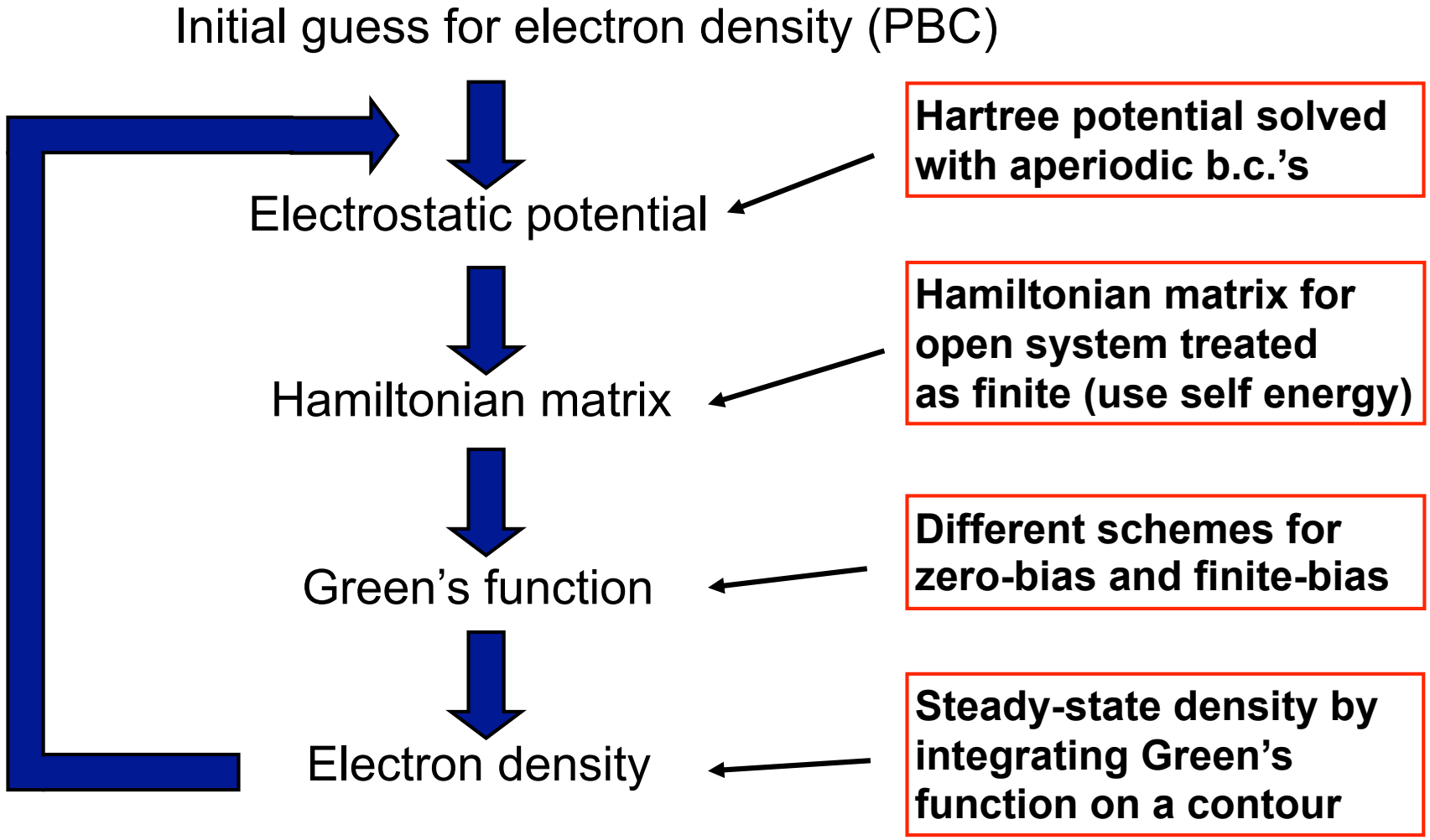
H_{DFT} =



$$\begin{pmatrix} H_L & V_{LC} & \\ V_{LC} & H_C & V_{CR} \\ & V_{CR} & H_R \end{pmatrix}$$

Reduce to finite size using self energy: $\hat{H} \rightarrow \hat{H}_C + \hat{\Sigma}$

First-Principles DFT-NEGF Workflow



After convergence:

Transmission obtained from Green's function and self-energies

Green's function and the density

zero-bias

$$\mathbf{D} = -\frac{1}{\pi}\mathrm{Im}\left[\int_{-\infty}^{\infty} d\epsilon\, \mathbf{G}(\epsilon + i\delta) n_F(\epsilon - \mu)\right].$$

finite-bias

$$\mathbf{D}_{\mu\nu} = w_{\mu\nu}(\mathbf{D}^L_{\mu\nu} + \Delta^R_{\mu\nu}) + (1 - w_{\mu\nu})(\mathbf{D}^R_{\mu\nu} + \Delta^L_{\mu\nu}),$$

$$\mathbf{D}^R_{\mu\nu} = -\frac{1}{\pi}\mathrm{Im}\left[\int_{EB}^{\infty} d\varepsilon\, \mathbf{G}(\varepsilon + i\delta)\, n_F(\varepsilon - \mu_R)\right],$$

$$\Delta^L_{\mu,\nu} = \int_{-\infty}^{\infty} d\varepsilon\, \rho^L_{\mu\nu}(\varepsilon)[n_F(\varepsilon - \mu_L) - n_F(\varepsilon - \mu_R)]$$

N_{eq} energy grid

$2*N_{eq}+N_{neq}$ energy grid

$$\mathbf{G}(E) = [E\mathbf{S} - \mathbf{H}_C - \mathbf{\Sigma}_L(E) - \mathbf{\Sigma}_R(E)]^{-1}$$

$$\rho^L_{\mu\nu}(\varepsilon) = \frac{1}{\pi}[\mathbf{G}(\varepsilon)\mathbf{\Gamma}_L(\varepsilon)\mathbf{G}^\dagger(\varepsilon)]_{\mu\nu}$$

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

extra step: triple product

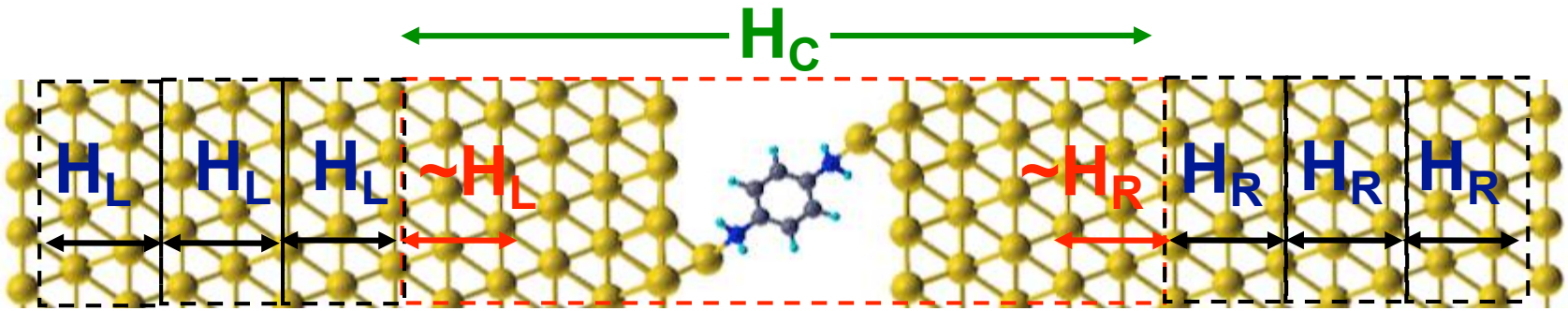
total time ~ N_{eq}

30 ~ 40 SCF cycles,
each cycle 10 ~ 15 mins

total time ~ $2N_{eq} + N_{neq}$ + 2(triple product)

100 ~ 150 SCF cycles,
each cycle 30mins ~ 1hour

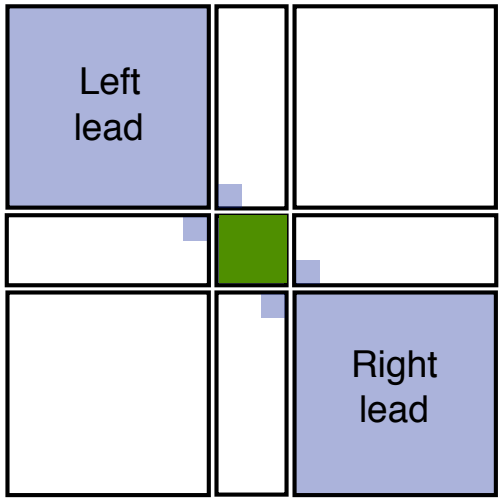
Conductance from Landauer formula & DFT+Σ

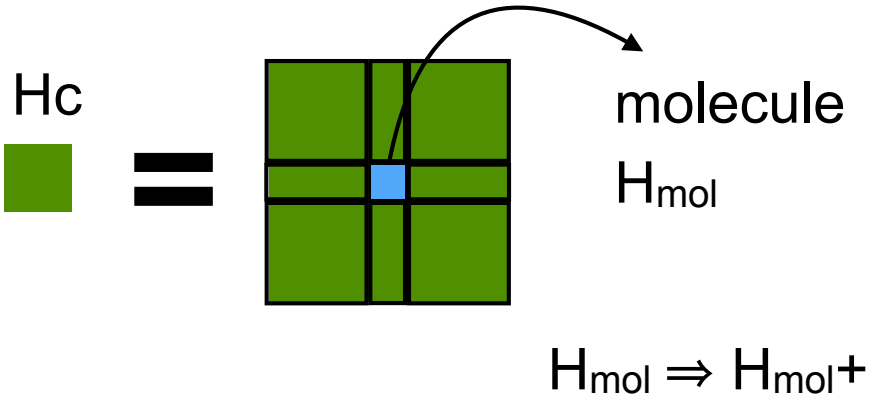


$$g = \frac{2e^2}{h}\, T(E)\big|_{E=E_F} = \mathrm{Tr}\left[\Gamma_L G \Gamma_R G^\dagger\right](E)\big|_{E=E_F}$$

- All quantities are of dimension **Nc**. Typically use ~10^2 energy grid
- NSCF: takes same time for zero/finite bias

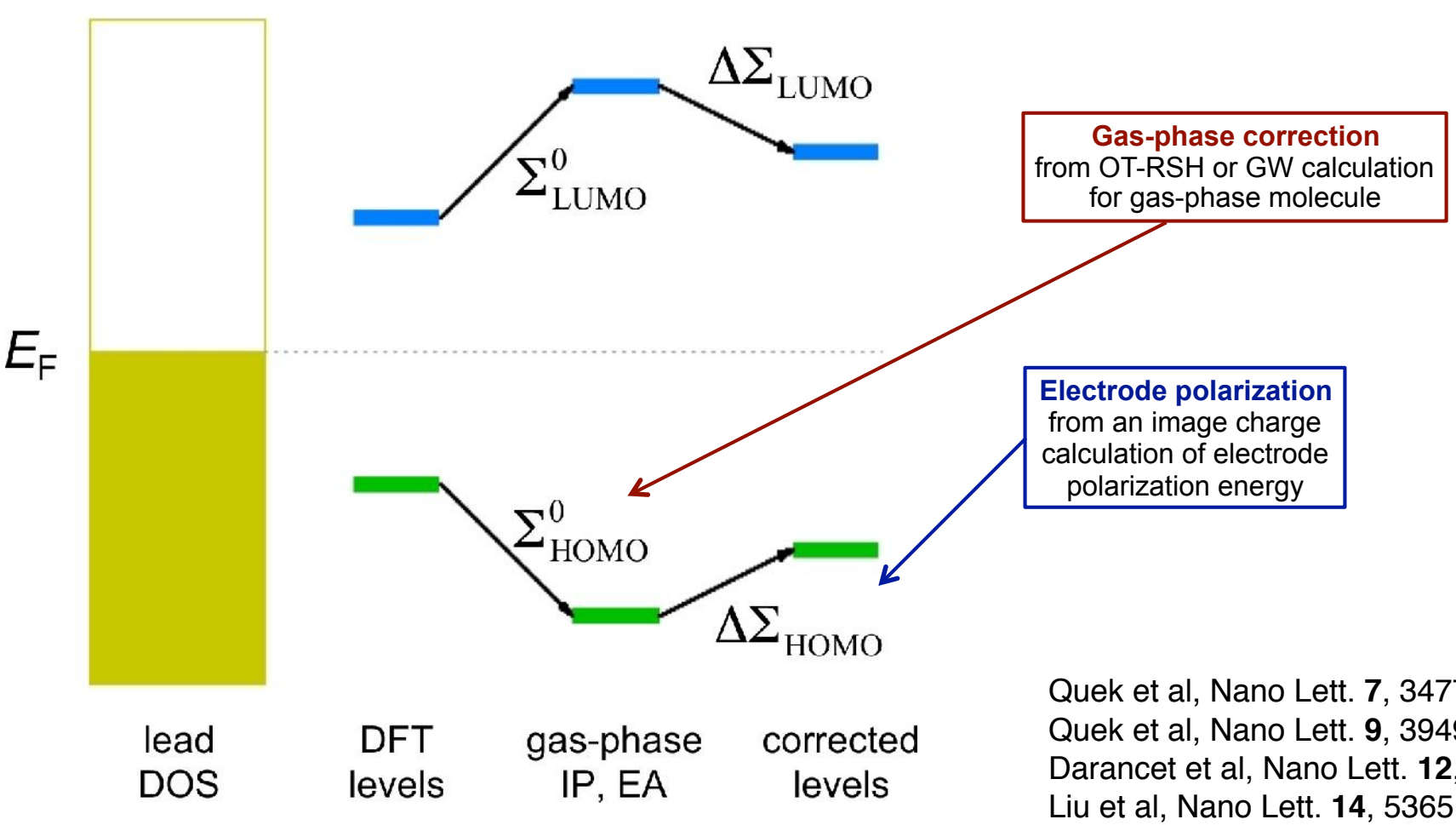
DFT+Σ:





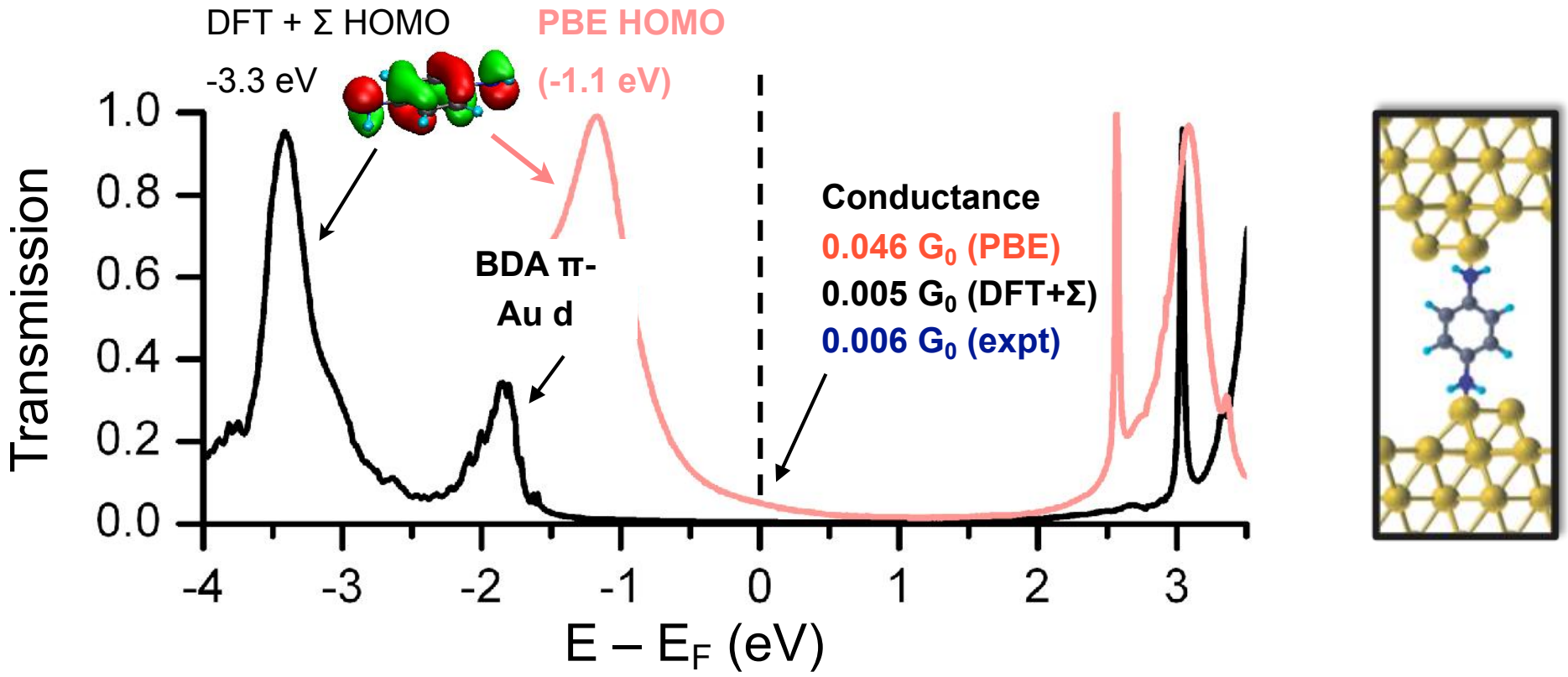
DFT+Σ: Model GW Self-Energy Correction

- 'One-shot' correction $$H_c \rightarrow H_c + \sum_{\mathrm{mol}} \Sigma_{\mathrm{mol}} |\psi_{\mathrm{mol}}\rangle\langle\psi_{\mathrm{mol}}|$$
- Two terms, no adjustable parameters



Quek et al, Nano Lett. **7**, 3477 (2007)
Quek et al, Nano Lett. **9**, 3949 (2009)
Darancet et al, Nano Lett. **12**, 6250 (2012)
Liu et al, Nano Lett. **14**, 5365 (2014)
Egger et al, Nano Lett. **15**, 2448 (2015)

Impact of Self-Energy Corrections: Benzene Diamine-Au



- Better treatment of exchange and correlation yields G_{theory} within <20% of G_{expt} !

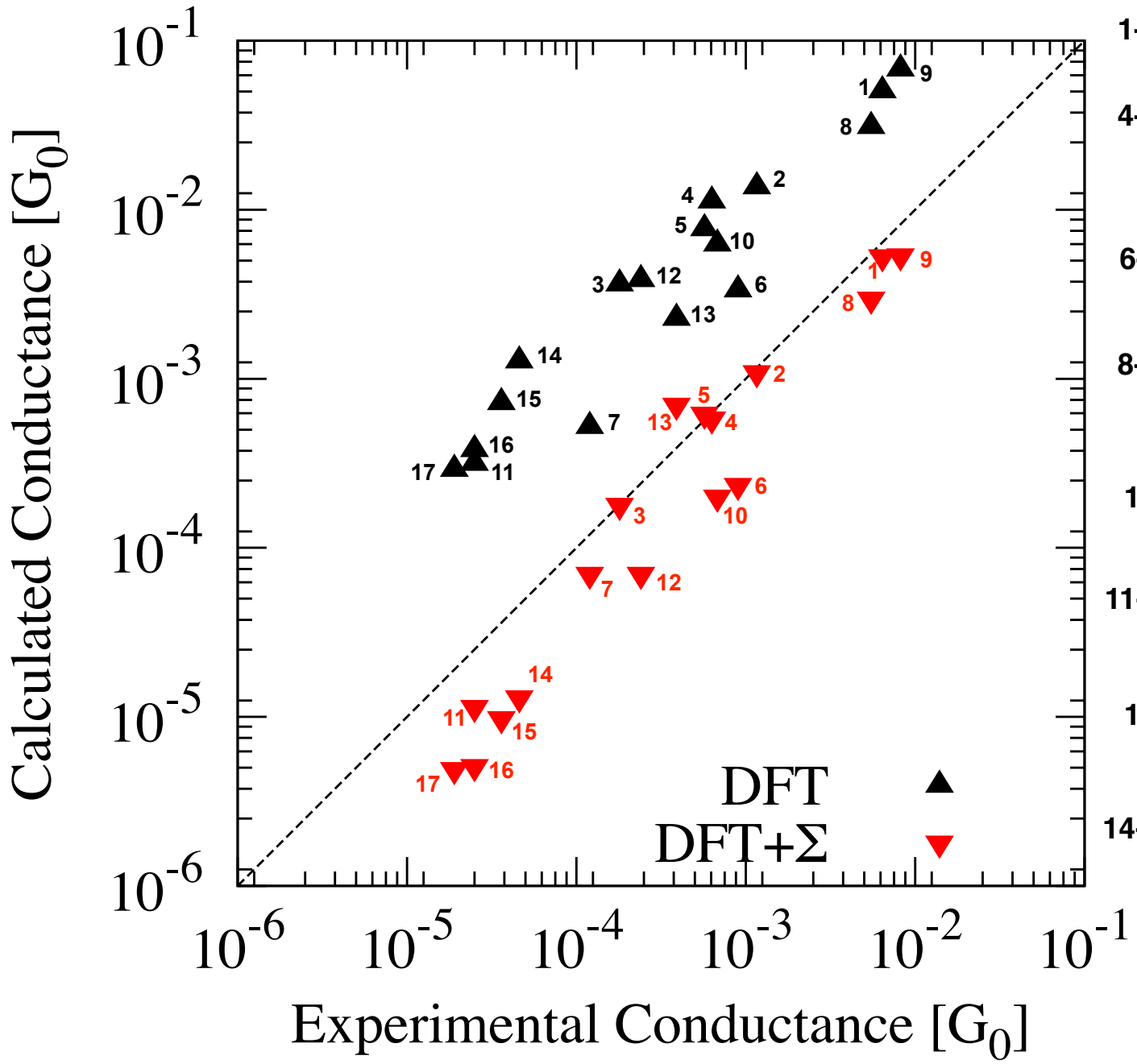
$G_{GW} = 0.02\text{-}0.004G_0$

Strange et al, Phys. Rev. B. **83**, 115108 (2011)
Rangel et al, Phys Rev. B. **84**, 045426 (2011)

Quek *et al*, Nano Lett. **7**, 3477 (2007)

Quek *et al*, Nano Lett. **9**, 3949 (2009)

Molecular Junction Conductance: Experiment vs Theory

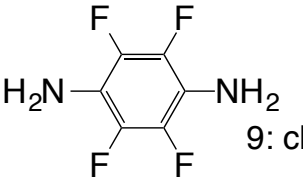


1-3 H_2N-(C$_6$H$_4$)$_n$-NH_2 n=1, 2, 3

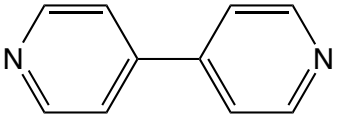
4-5 H_2N-C$_6$H$_4$-CH=CH-C$_6$H$_4$-NH_2

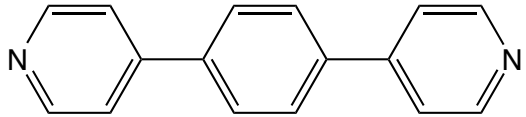
5: triple bond in the center

6-7 H_2N-$(CH_2)_n$-NH_2 n=4, 6

8-9 

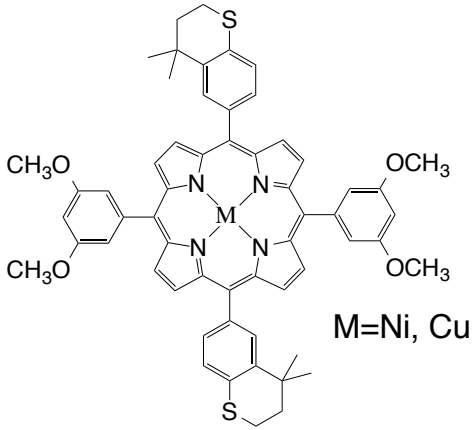
9: change -F to -CH_3

10 

11-12 

12: change benzene to C=C

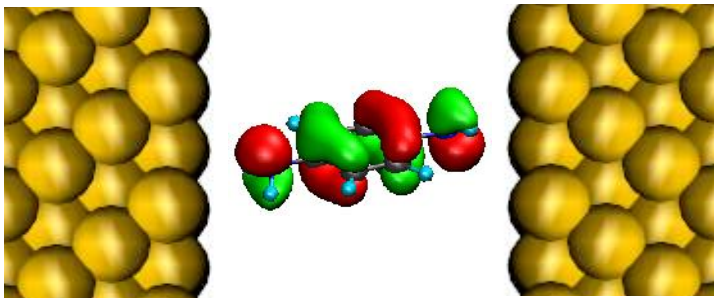
13 Ph_2P-$(CH_2)_3$-PPh_2

14-17 

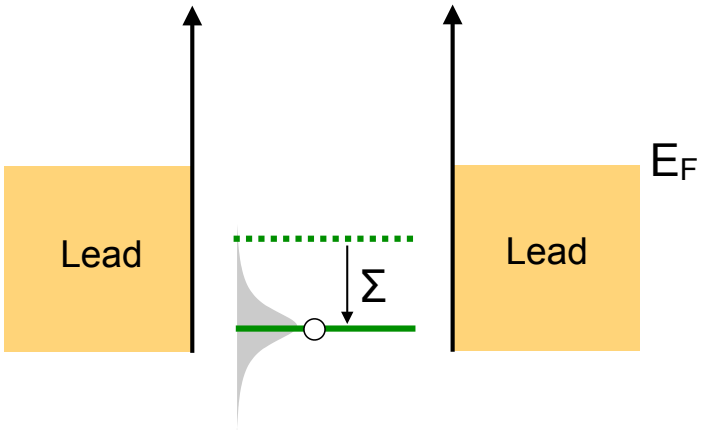
M=Ni, Cu, Co, 2H

Validity of DFT+Σ, an approx. GW approach

- **"Weakly coupled" junctions:**
  - ➡ Molecular states unchanged in junction
  - ➡ Frontier orbitals are far from E_F
  - ➡ Substrate polarization treated with image charge physics



- **Neglect**
  - ➡ Charge transfer between molecule & lead
  - ➡ Changes in molecular polarizability
  - ➡ Lead eigenstate self-energy corrections



Incorporating DFT+Σ Physics into a Hybrid Functional

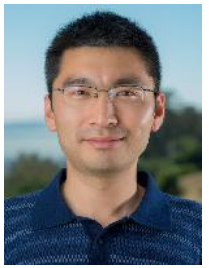
Optimally-Tuned Range-Separated Hybrid (OTRSH) Functional:

$$\frac{1}{r} = \frac{\alpha + \beta \mathrm{erf}(\gamma r)}{r} + \frac{1 - [\alpha + \beta \mathrm{erf}(\gamma r)]}{r}$$

treated using non-local Fock exchange

Challenging for plane-waves!

treated using semi-local DFT exchange



Gas-phase molecule:

- α+β=1, and usually choose α=0.2;
- tune γ to satisfy IP-theorem.

Molecular Crystal:

- use gas-phase α and γ;
- α+β = 1/ε < 1.

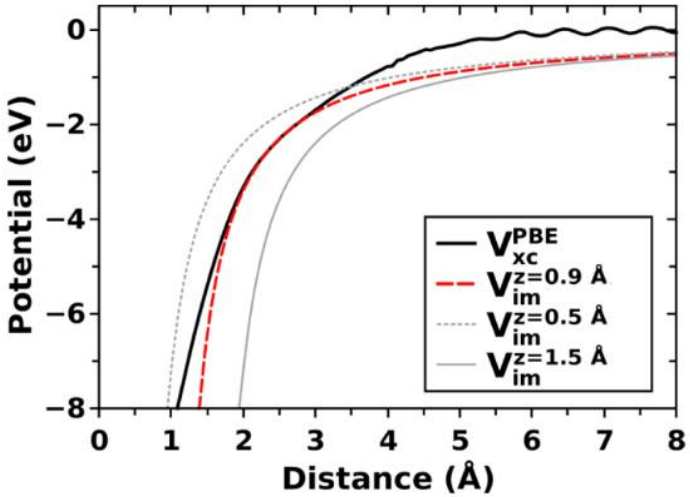
Refaely-Abramson, Sharifzadeh, Govind, Autschbach, Neaton, Baer, and Kronik, Phys. Rev. Lett. **109**, 226405 (2012).
Refaely-Abramson, Sharifzadeh, Jain, Baer, Neaton, and Kronik, Phys. Rev. B **88**, 081204(R) (2013).

Optimally-Tuned RSH Functional for Interfaces

For a specific molecule-metal interface:

❶ Use gas-phase molecular α and γ;

❷ For the metal slab, find the image plane z_0:

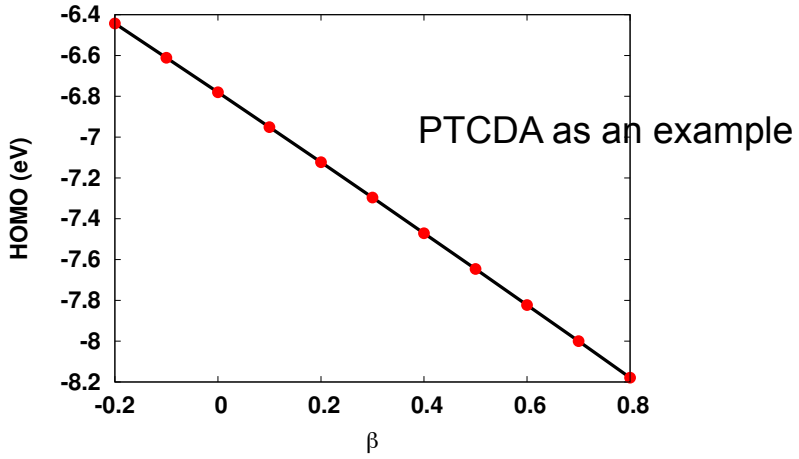


Egger, Liu, Neaton, and Kronik, Nano Lett. **15**, 2448 (2015).

❸ Compute image-charge interaction $P = \dfrac{1}{4|z - z_0|}$

❹ Tune β such that:

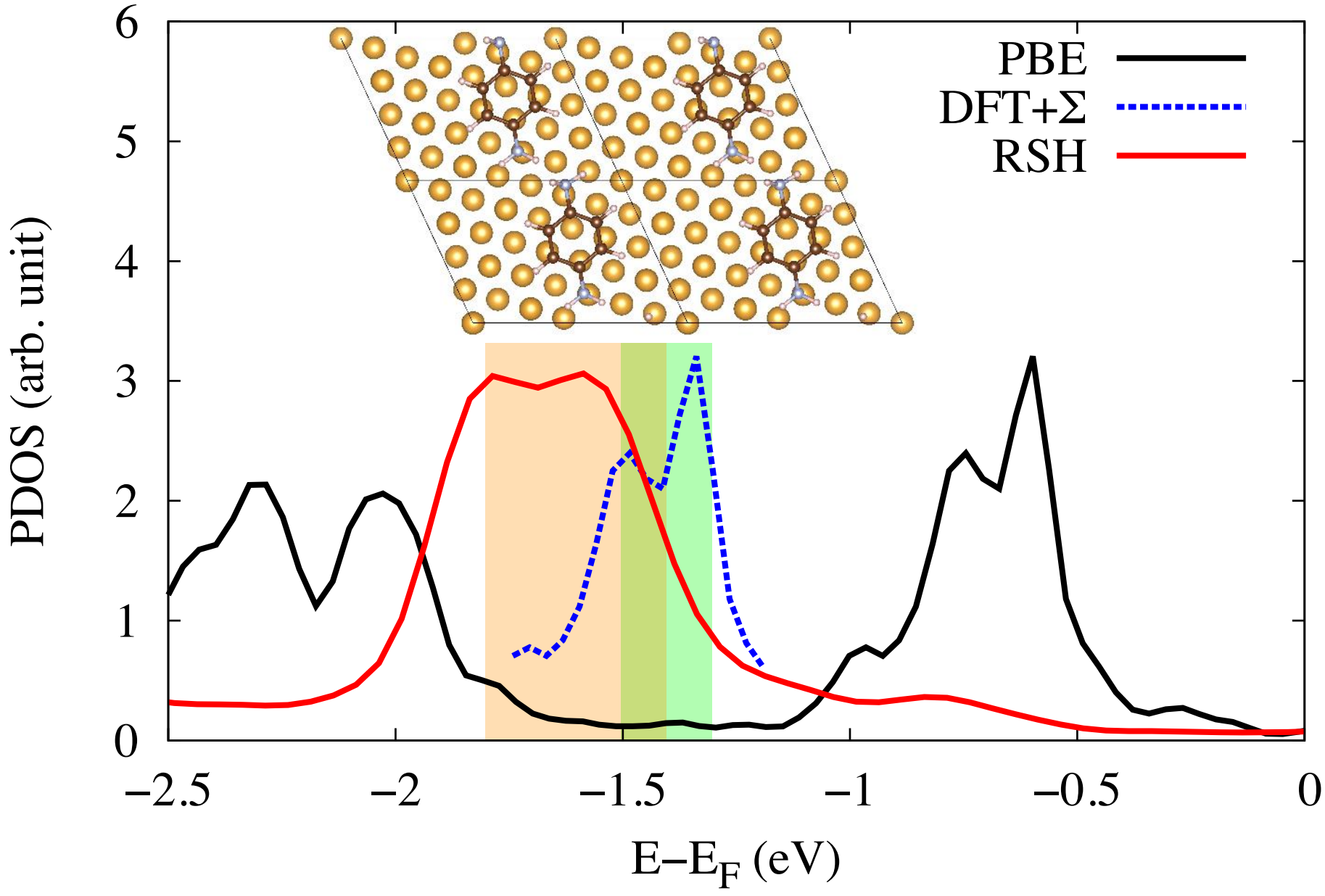
$$\varepsilon_{\mathrm{H}}(\beta) - \varepsilon_{\mathrm{H}}(\beta_0) = P$$



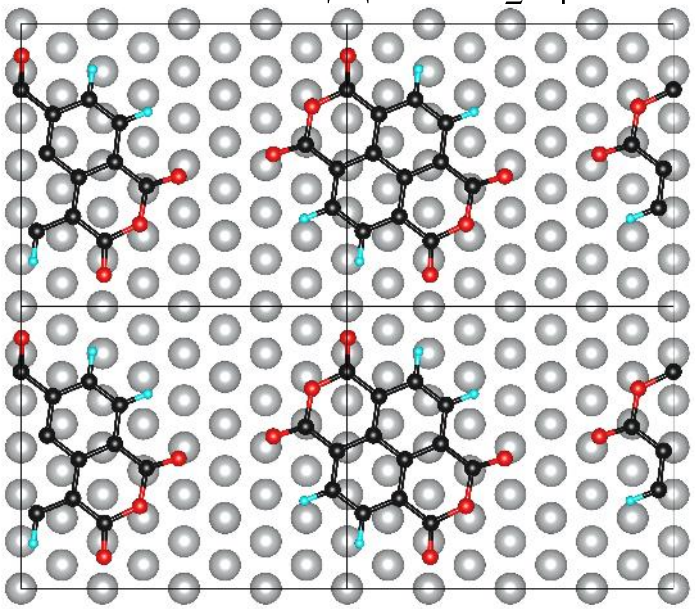
Currently only implemented for norm-conserving pseudopotential.

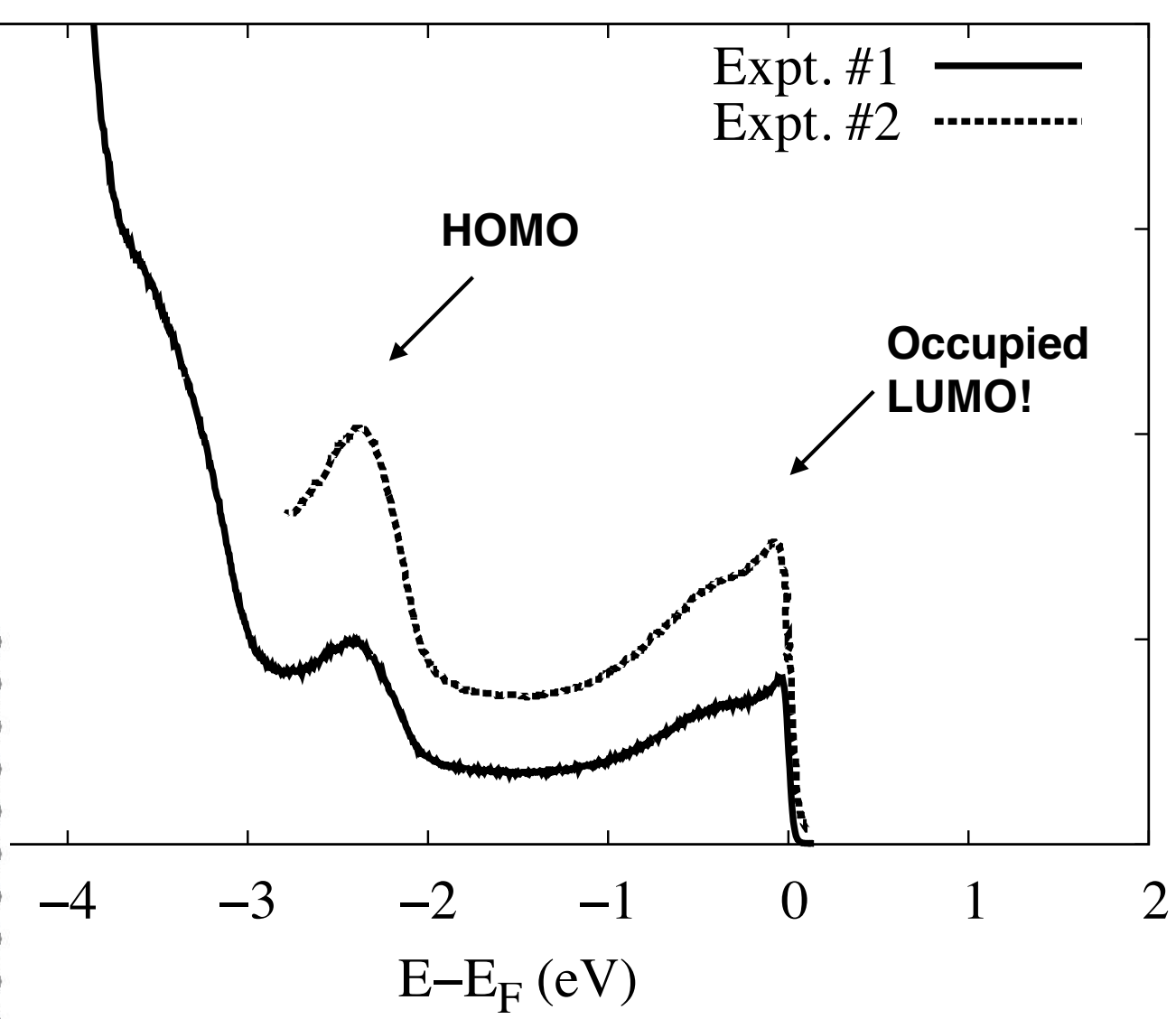
Liu, Egger, Refaely-Abramson, Kronik, and Neaton, in prep. (2016).

BDA @ Au(111): RSH Predicts Deeper Level & Different Lineshape



NTCDA @ Ag(111): Level Alignment with Partially Occupied States





expt1: A. Schöll, *et al*, Science, **329**, 303 (2010)

expt2: J. Ziroff, *et al*, Phys. Rev. B **85**, 161404(R) (2012)

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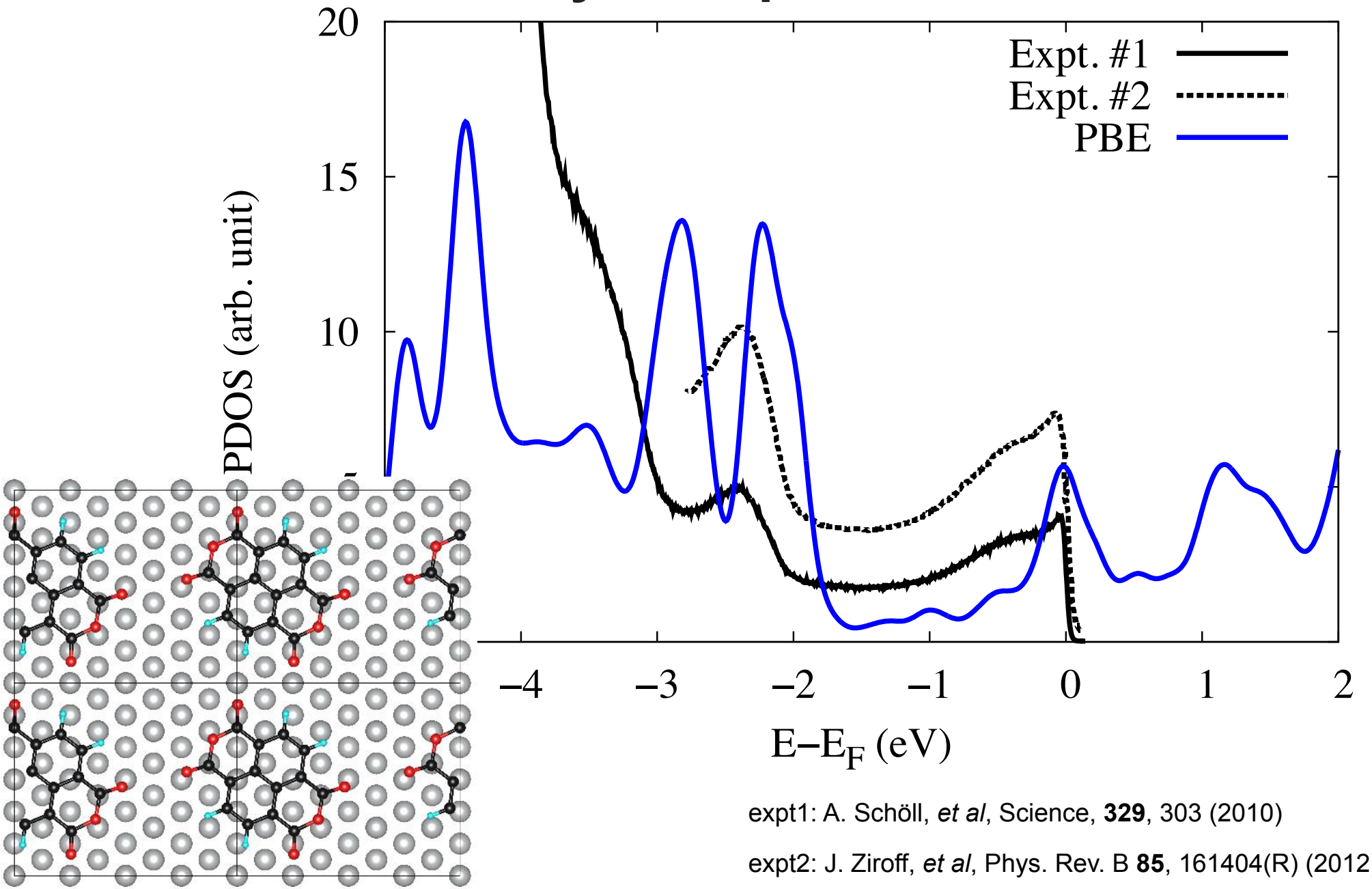

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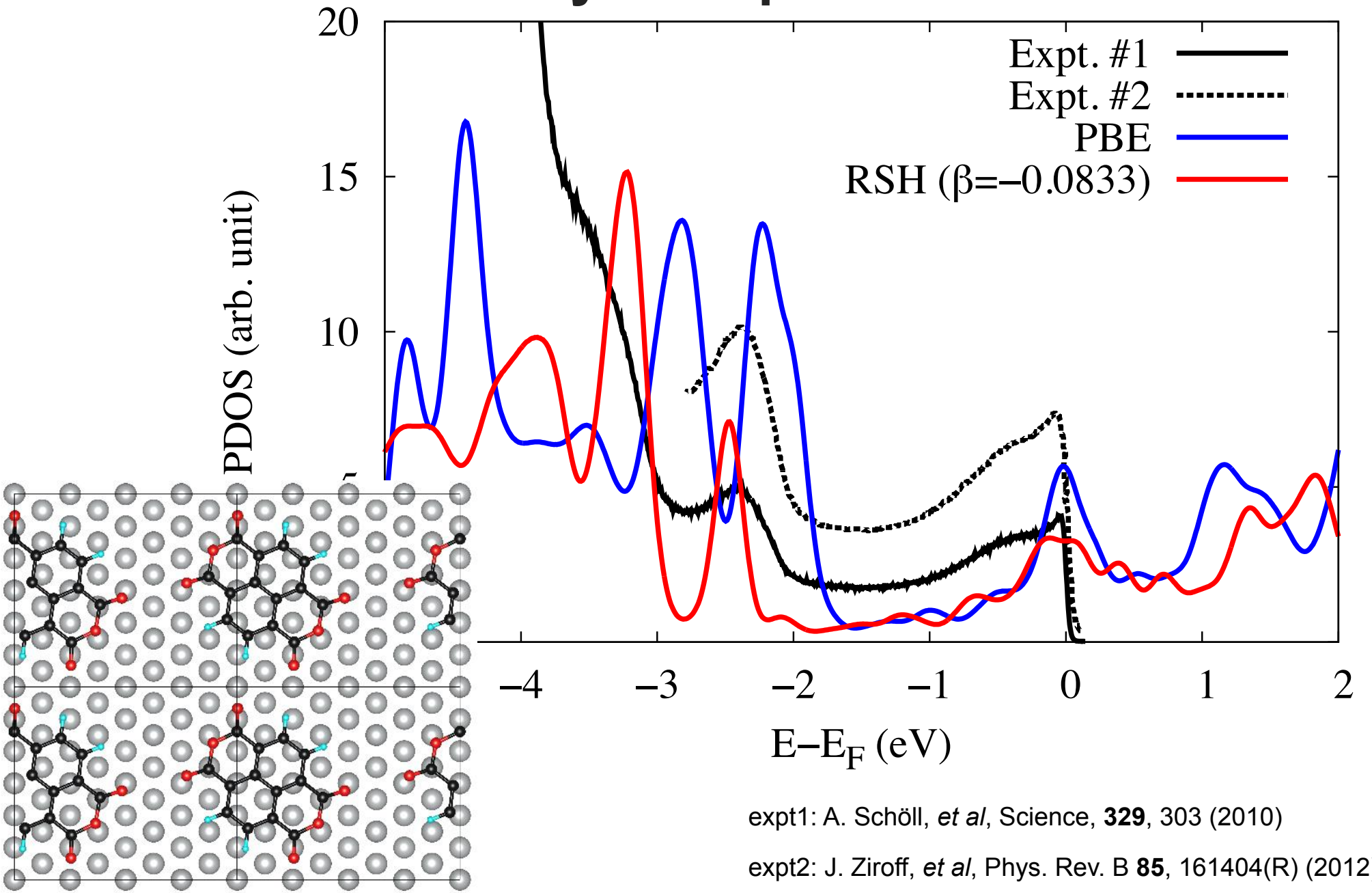
NTCDA @ Ag(111): Level Alignment with Partially Occupied States

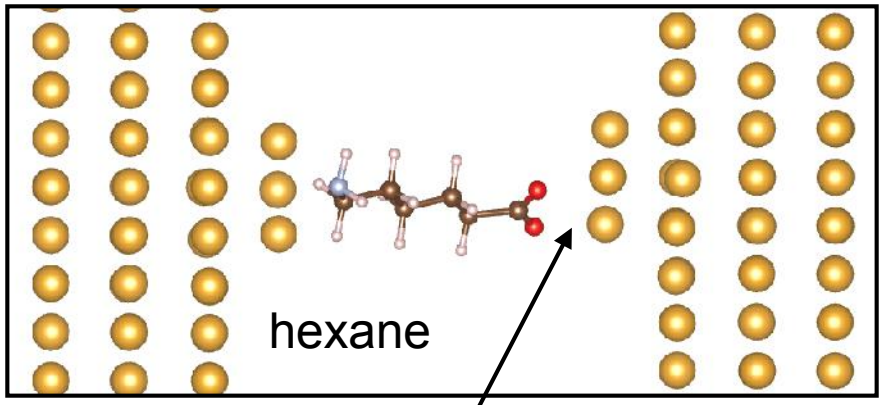


expt1: A. Schöll, *et al*, Science, **329**, 303 (2010)

expt2: J. Ziroff, *et al*, Phys. Rev. B **85**, 161404(R) (2012)

OT-RSH Applied to Molecular Junctions

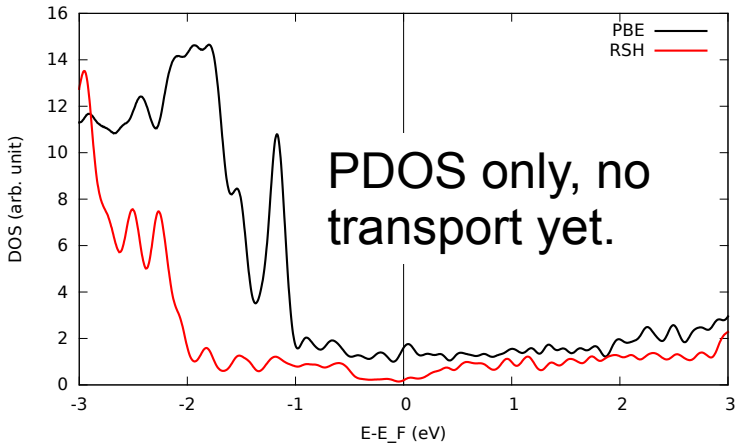
Transport with peptides - need to understand how -COOH binds to Au surface.
Study the difference between peptides and alkanes on decay constant β: g ~ exp(-βL).



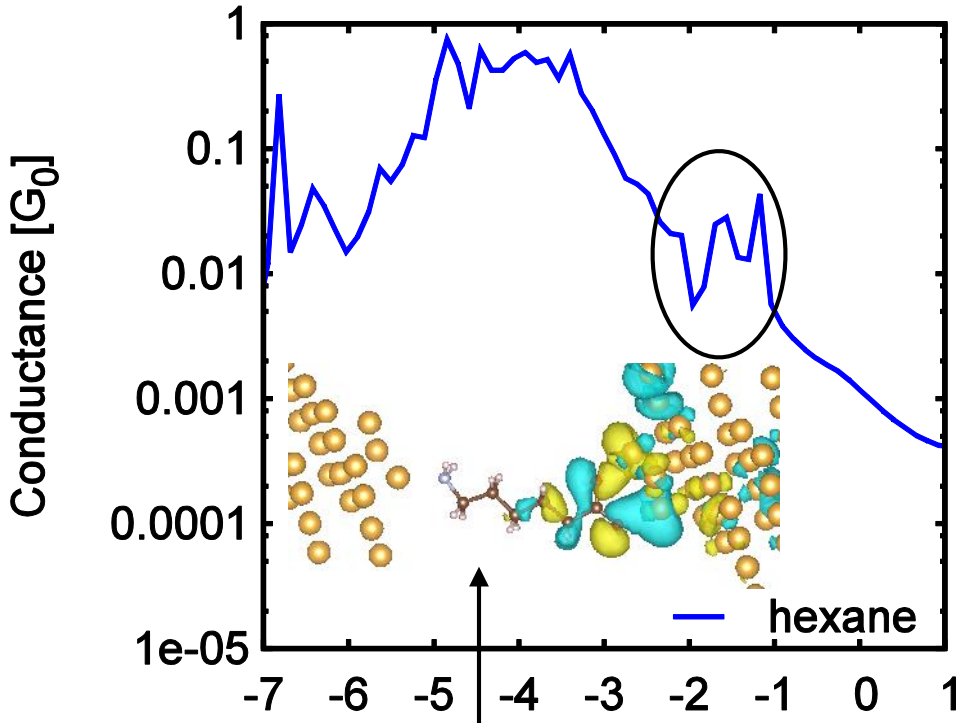
-COO binding

no obvious gas-phase reference

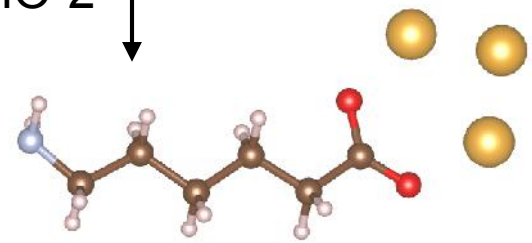
DFT+Σ does not directly apply



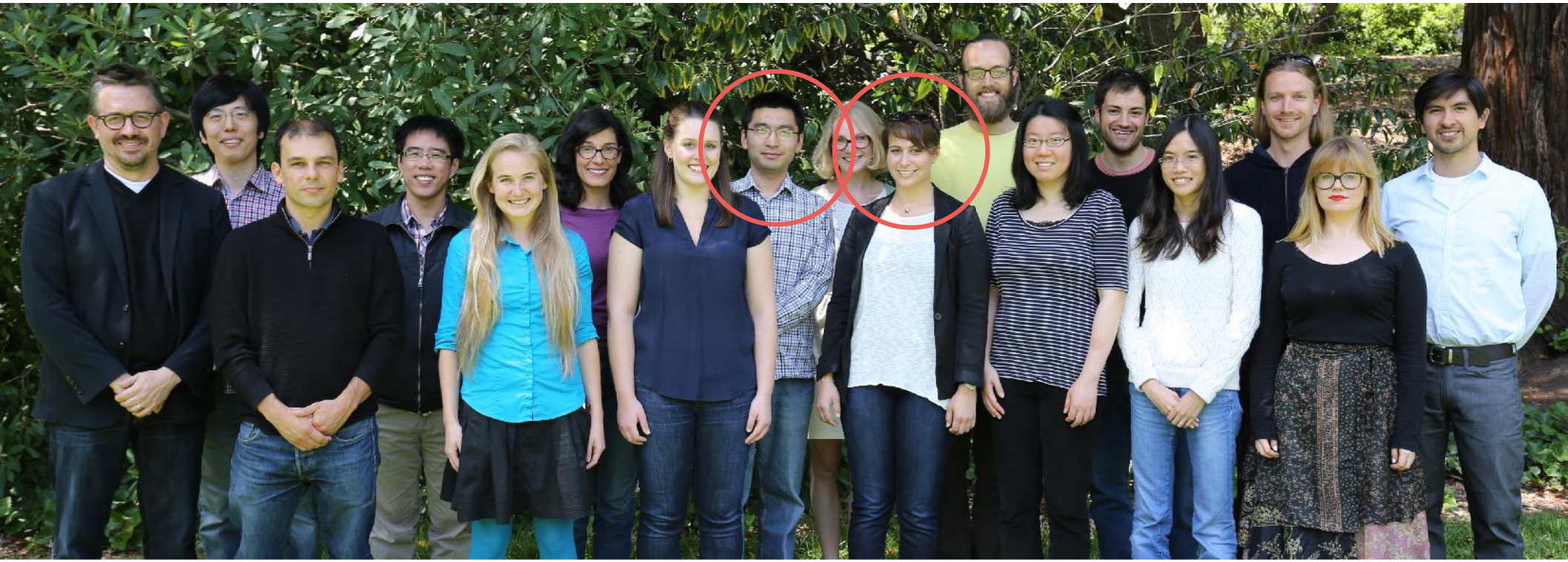
Refaely-Abramson, Liu, Neaton et al., in prep.



eigenchannel ~ HOMO-2



A different reference: mol + 3Au



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