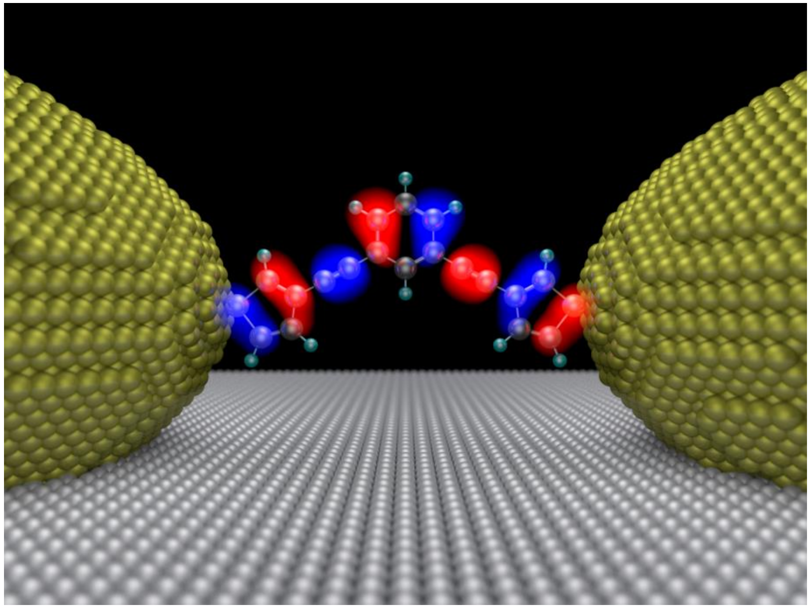
UNI BASEL

Empa
Materials Science and Technology

SNI
SWISS NANOSCIENCE INSTITUTE
EINE INITIATIVE DER UNIVERSITÄT BASEL UND DES KANTONS AARGAU

Molecular and carbon-based electronic systems

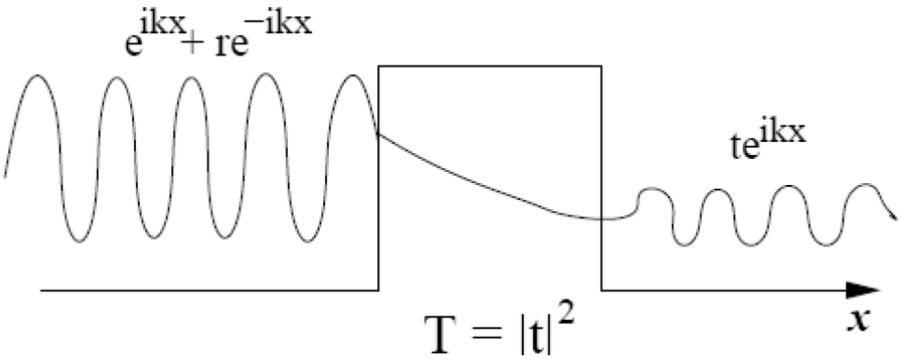
Lecture 9 - Insights in density functional theory for molecular junctions

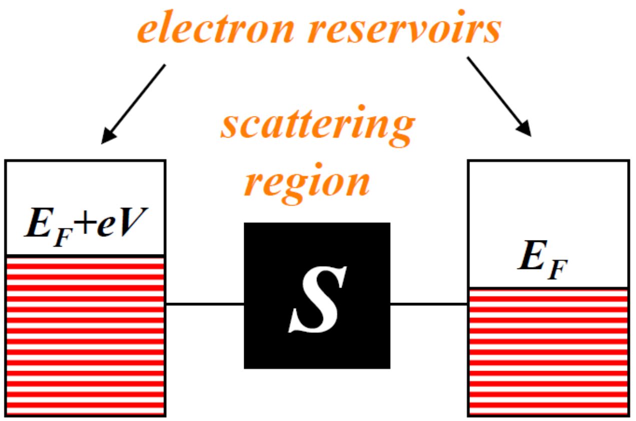


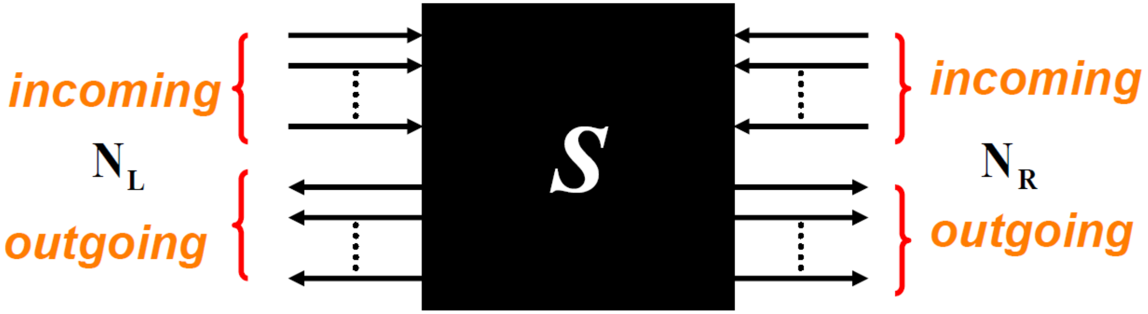
Vorlesung Uni Basel, HS2017

Landauer approach to electron transport

Electronic transport as scattering problem







$$G = \frac{2e^2}{h} T(E_F)$$

G = conductance

$T(E_F)$ = transmission at the Fermi energy

see Cuevas, Molecular Electronics, World Scientific

R. Landauer, IBM J. Res. Dev. 1, 223 (1957)

simple one-level model

Analytical expression for the current

$$I(E,V) = \frac{2e}{h} \int^{\infty} T(E,V)[f(E-\mu_2) - f(E-\mu_1)]dE$$

At low T , Fermi functions ≈ Heaviside step functions, and

$$I(V) = \frac{2e}{h} \int_{\frac{-eV}{2}}^{\frac{eV}{2}} T(E,V)dE$$

Using the expressions

$$T(E,V) = \frac{4\Gamma_1\Gamma_2}{(E - E_0(V))^2 + (\Gamma_1 + \Gamma_2)^2}$$

$$E_F(V) = \frac{eV}{2} \cdot \frac{\Gamma_1 - \Gamma_2}{\Gamma_1 + \Gamma_2}$$

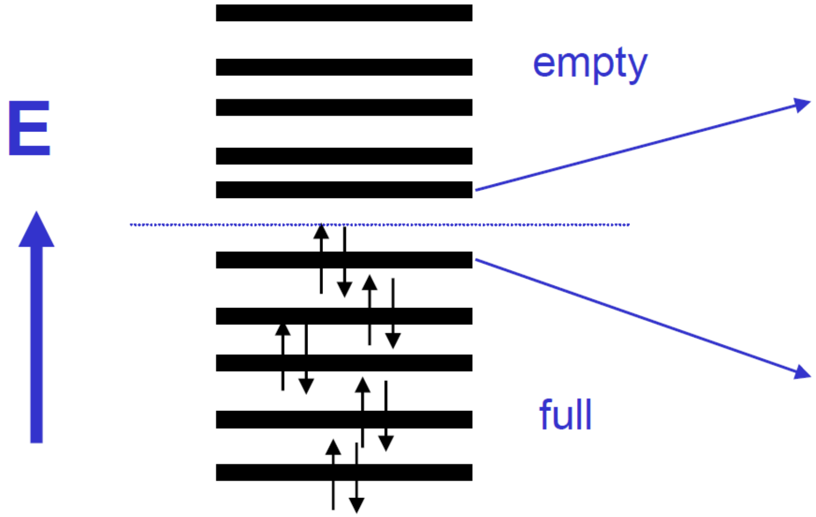
we can write

$$I(V) = \frac{8e}{h} \cdot \frac{\Gamma_L\Gamma_R}{\Gamma_L + \Gamma_R} \left[\arctan\left(\frac{2E_0 + eV\left(\frac{\Gamma_L - \Gamma_R}{\Gamma_L + \Gamma_R} + 1\right)}{2\left(\Gamma_L + \Gamma_R\right)} \right) - \arctan\left(\frac{2E_0 + eV\left(\frac{\Gamma_L - \Gamma_R}{\Gamma_L + \Gamma_R} - 1\right)}{2\left(\Gamma_L + \Gamma_R\right)} \right) \right]$$

3 fit parameters Γ_1, Γ_2, **$E_0 = E_0 (V)$**

molecular energy levels

(isolated) molecule
quantum system with spectrum of discrete energy states (molecular orbitals)



LUMO = lowest unoccupied molecular orbital

(HOMO-LUMO gap from light absorption)

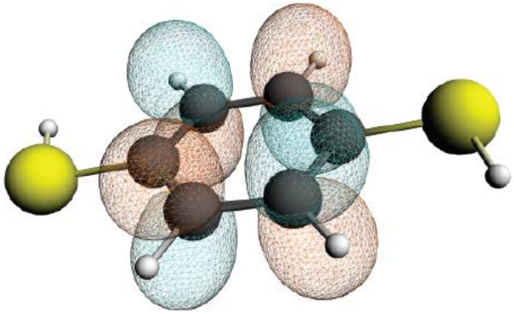
HOMO = highest occupied molecular orbital

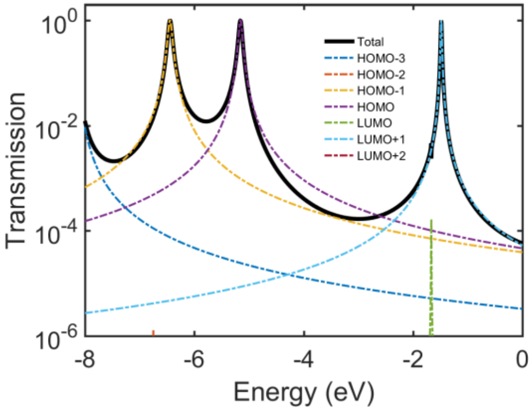
⇨ ‘Particle in a box’: molecule is small box

box smaller ⇔ levels more spaced ($\delta E > k_B T$)

Overview

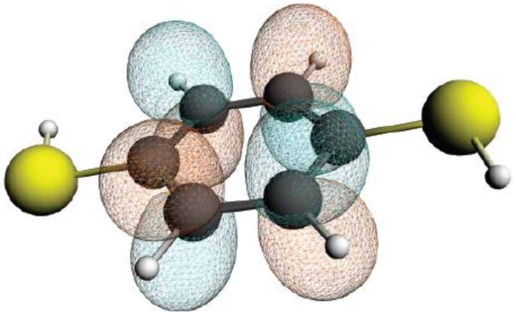
- Quantum chemistry (QC)
- Density functional theory (DFT)
- Non-equilibrium Green's function (NEGF)



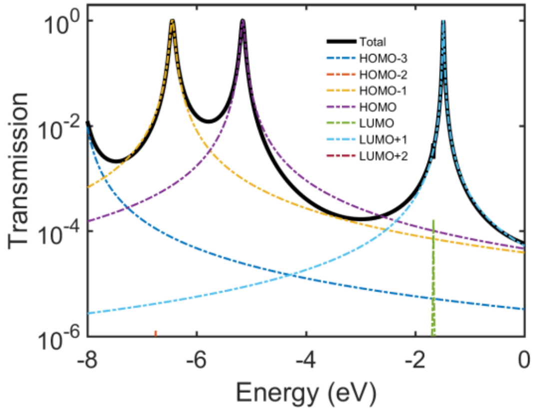


Overview

- Quantum chemistry (QC)

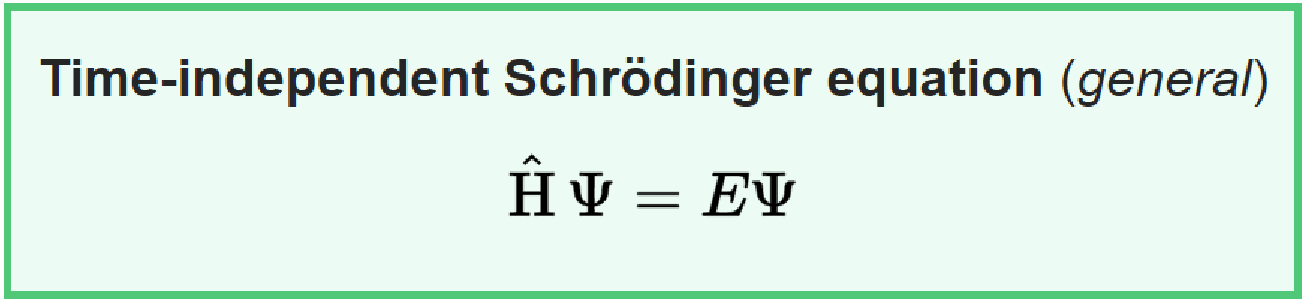


- Density functional theory (DFT)
- Non-equilibrium Green's function (NEGF)



Schrödinger’s Equation

- Molecule can be described using the Schrödinger Equation



Time-independent Schrödinger equation (*general*)

$$\hat{\mathrm{H}}\,\Psi = E\Psi$$

Schrödinger’s Equation

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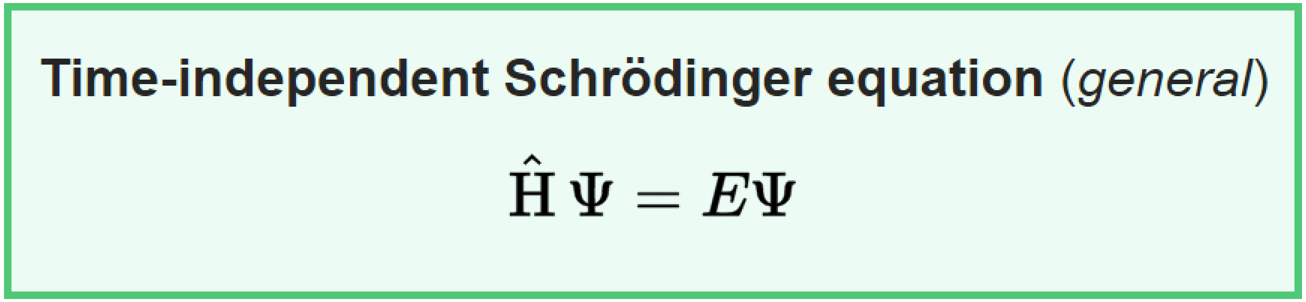

Time-independent Schrödinger equation (*general*)

$$\hat{\mathrm{H}}\,\Psi = E\Psi$$

$$\hat{H} = -\frac{\hbar^2}{2m_e}\sum_i \nabla_i^2 + \frac{1}{2}\sum_{i\neq j}\frac{e^2}{|\boldsymbol{r}_i - \boldsymbol{r}_j|} - \sum_{i,J}\frac{Z_J e^2}{|\boldsymbol{r}_i - \boldsymbol{R}_J|} - \sum_I \frac{\hbar^2}{2M_I}\nabla_I^2 + \frac{1}{2}\sum_{I\neq J}\frac{Z_I Z_J e^2}{|\boldsymbol{R}_I - \boldsymbol{R}_J|}$$

Very Complex many body Problem !!
(Because everything interacts)

Born-Oppenheimer approximation

- Electrons are much lighter, and faster

- Decoupling in the wave function

$$\Psi(\vec{\boldsymbol{r}}, \vec{\boldsymbol{R}}) \approx \Psi_e(\vec{\boldsymbol{r}})\Psi_n(\vec{\boldsymbol{R}})$$

- Nuclei described as constant external potential

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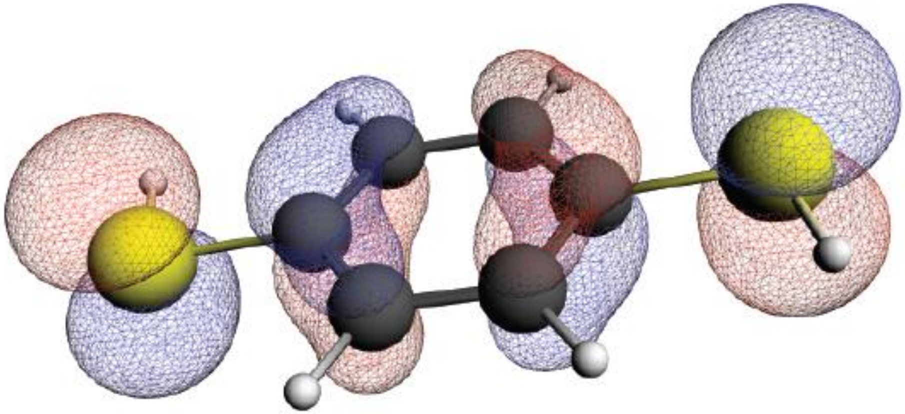
- Nuclei described as constant external potential

- Still numerically intractable

$$\hat{H} = -\frac{\hbar^2}{2m_e}\sum_i \nabla_i^2 + \frac{1}{2}\sum_{i\neq j}\frac{e^2}{|\boldsymbol{r}_i - \boldsymbol{r}_j|} - \sum_{i,J}\frac{Z_J e^2}{|\boldsymbol{r}_i - \boldsymbol{R}_J|}$$

Quantum chemistry calculations

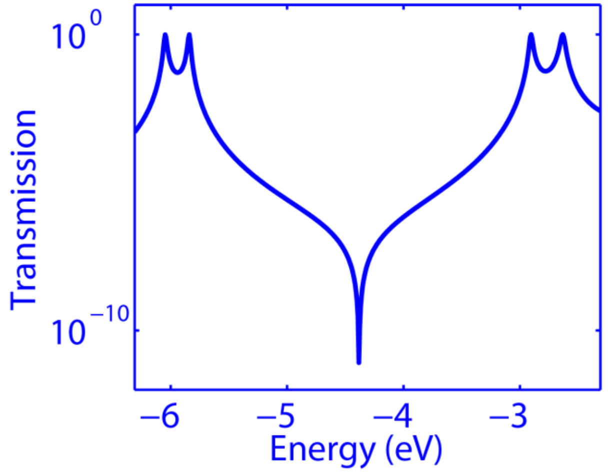


Electronic structure

- Numerical renormalization group
- Configuration interaction
- Hartree Fock
- Density functional theory
- Hückel method

Transport

- NEGF
- GW



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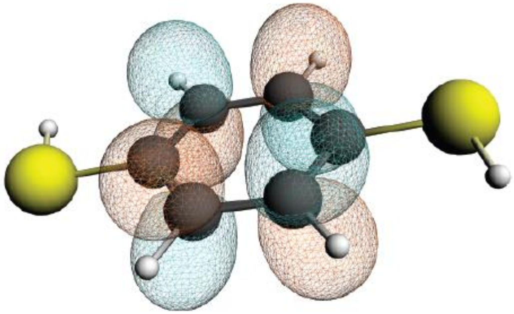
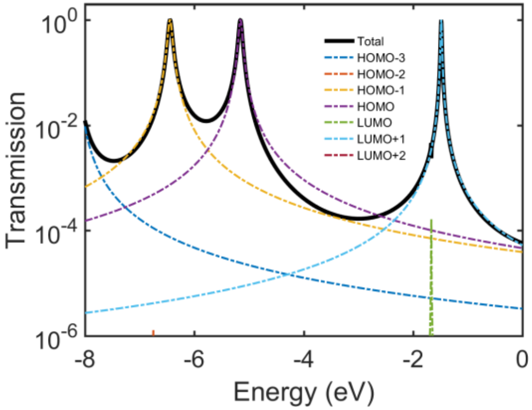


- Density functional theory (DFT)

- Non-equilibrium Green's function (NEGF)



DFT

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  - →equivalent independent single-particle problem

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  →equivalent independent single-particle problem

- The wave-function is a unique functional of the density (**1^e Hohenberg-Kohn theorem, 1964**)

- All system properties are governed *only* by the ground-state density.

- Nobelprize in 1998!

DFT

- The density n(r) which minimizes E[n(r)] is the ground-state density, and minimization of this functional alone is enough to fully determine the exact ground-state energy and density $n_0(r)$. **(2^e Hohenberg-Kohn theorem, 1964)**

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$$E_{\mathrm{KS}} = T_s[n] + \int \mathrm{d}^3 r\, V_{\mathrm{ext}}(\boldsymbol{r}) n(\boldsymbol{r}) + E_H[n] + E_{\mathrm{II}} + E_{\mathrm{xc}}[n]$$

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Kinetic energy

Electron-nuclei interaction

Electron-electron interaction

Ion-Ion interaction

Exchange + correlations

$$E_H[n] = \frac{1}{2} \int \mathrm{d}^3 r \int \mathrm{d}^3 r' \; \frac{n(\boldsymbol{r}) n(\boldsymbol{r}')}{|\boldsymbol{r} - \boldsymbol{r}'|}$$

Kohn-Sham equations

- But T_s and E_{XC} are unknown. How to find T_s ?

Kohn-Sham equations

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- Kohn and Sham proposed to model electrons as non-interacting particles that generate the same density as the interacting particles (mean field, 1965)

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + v_{\rm eff}(\mathbf{r})\right)\phi_i(\mathbf{r}) = \varepsilon_i\phi_i(\mathbf{r})$$

Exchange-correlation (XC)

- All we know about the functional E_{xc} is that it exists, however, its form is unknown.

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Local density approximation (LDA) : uniform electron gas: $E_{XC}[\rho]$

Generalized gradient approximation (GGA) : $E_{XC}(\rho,\nabla\rho)$

Hybrid (B3LYP) : including some HF for exchange

Dispersion/long-range corrected functionals

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Local density approximation (LDA) : uniform electron gas: $E_{XC}[\rho]$
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Hybrid (B3LYP) : including some HF for exchange
Dispersion/long-range corrected functionals

→As the XC functional is not exact, electron exchange and correlations are not taken properly into account.

Basis set used to describe orbitals

- A **basis set** is a set of basis functions which are combined in linear combinations to create molecular orbital wave-functions.

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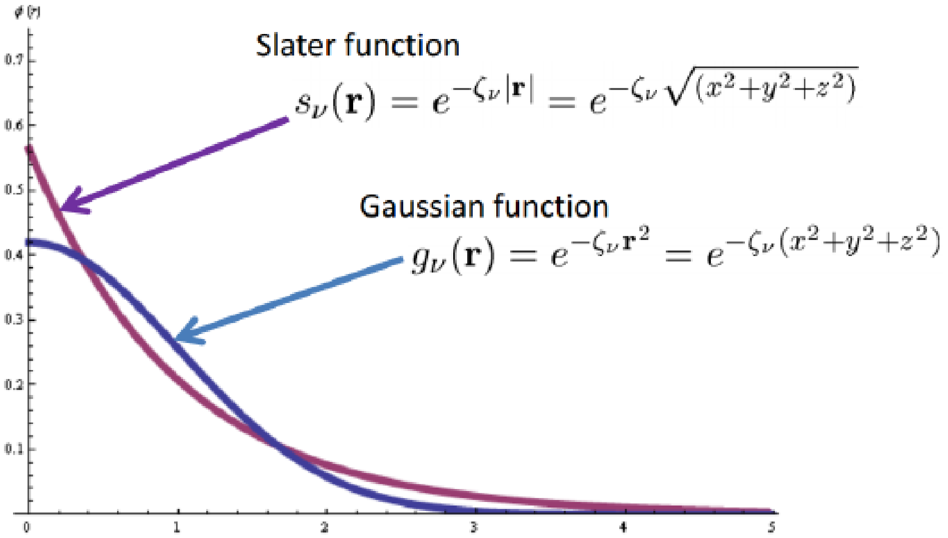
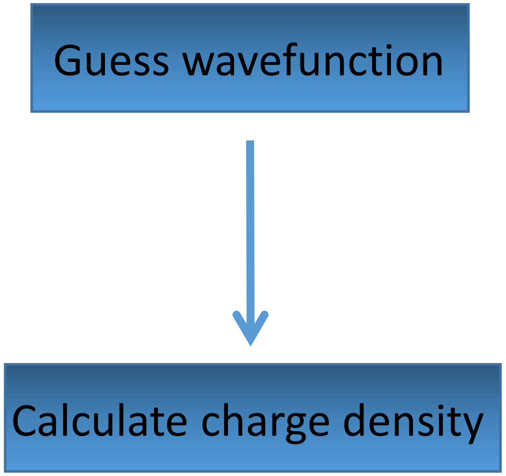
- Basis set can be any type of set of functions: atomic orbitals, plane waves, …



Convergence (SCF)

Guess wavefunction

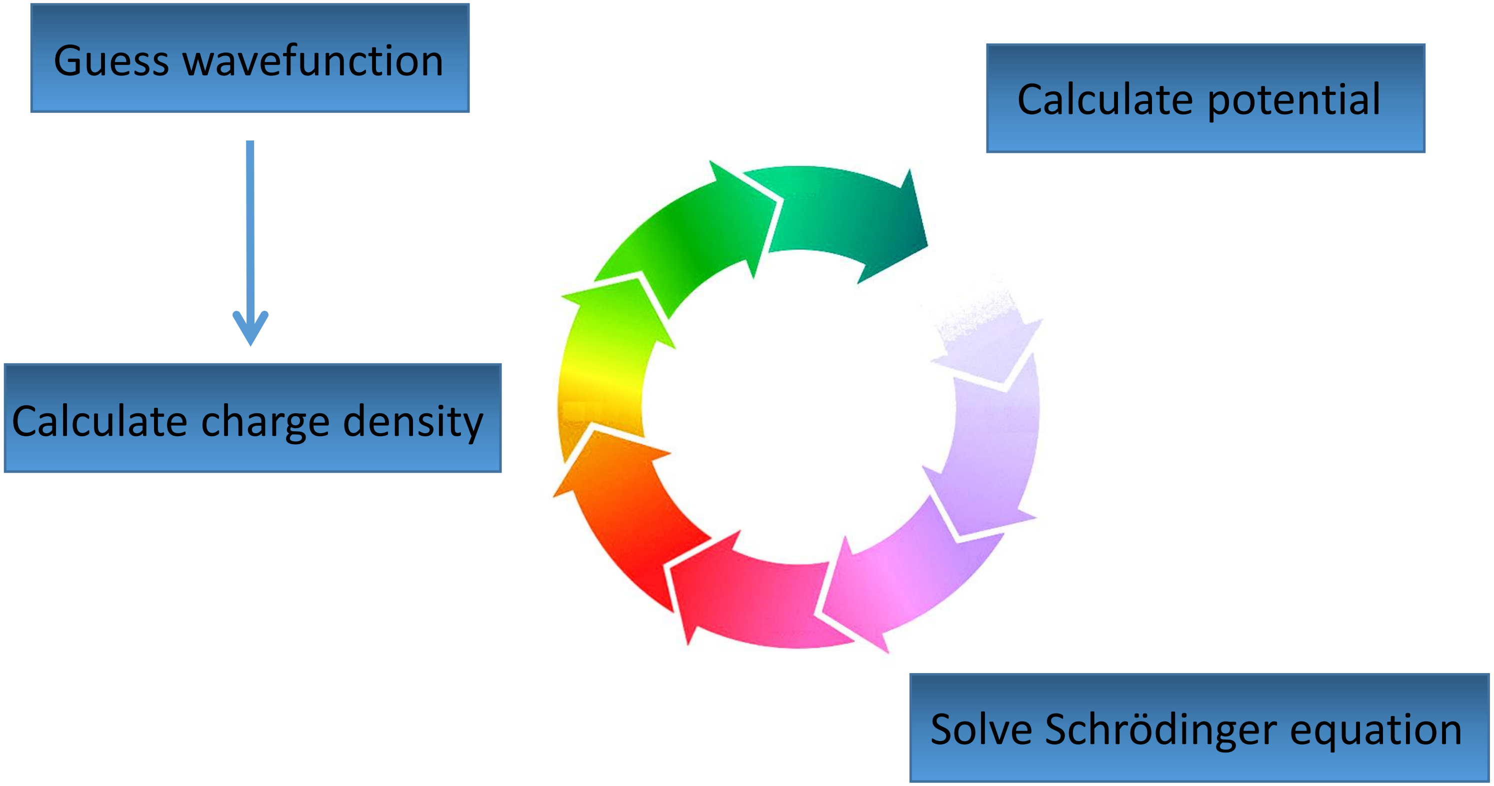
Convergence (SCF)



Guess wavefunction

Calculate charge density

Convergence (SCF)



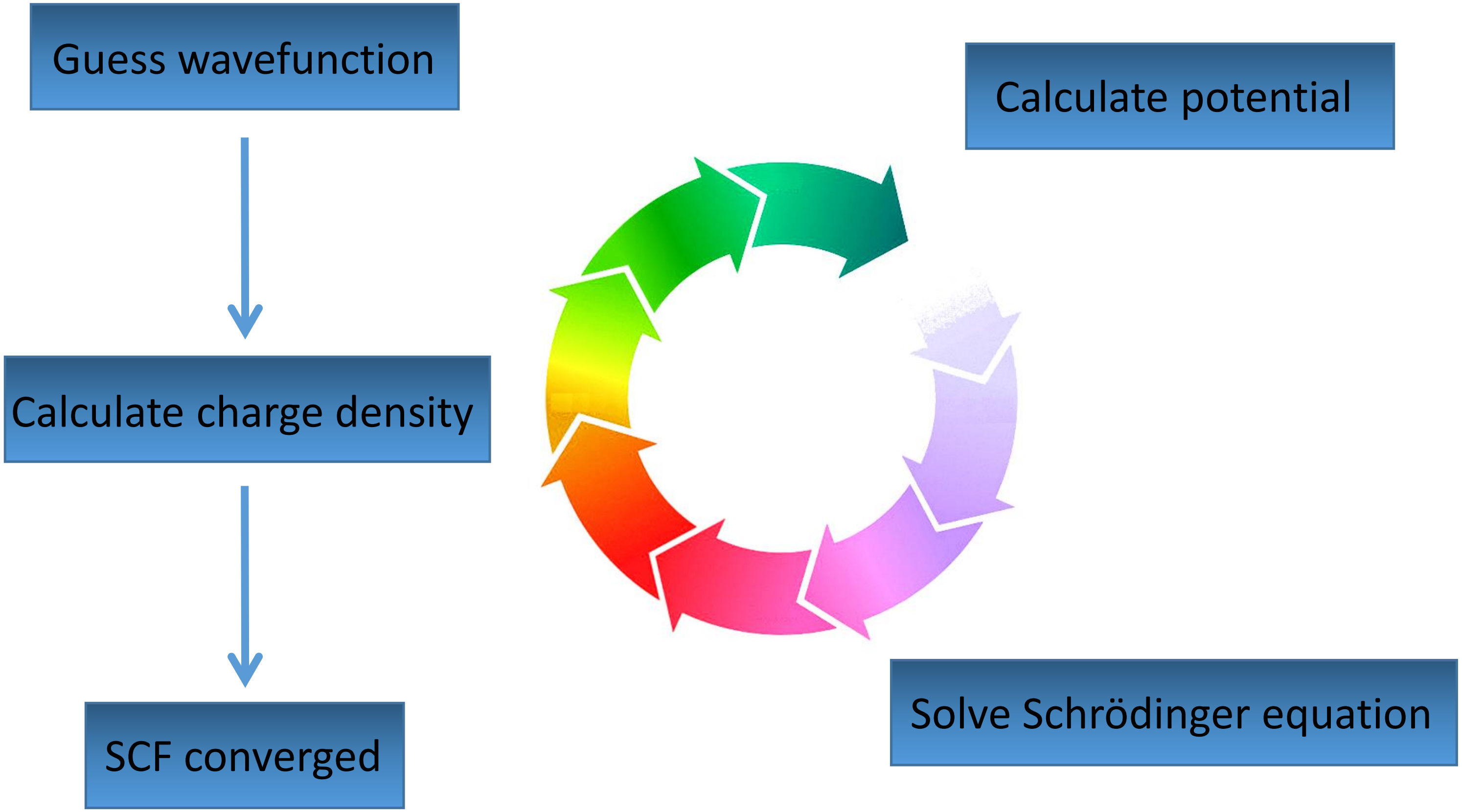
Guess wavefunction

Calculate charge density

Calculate potential

Solve Schrödinger equation

Convergence (SCF)



Guess wavefunction

Calculate charge density

SCF converged

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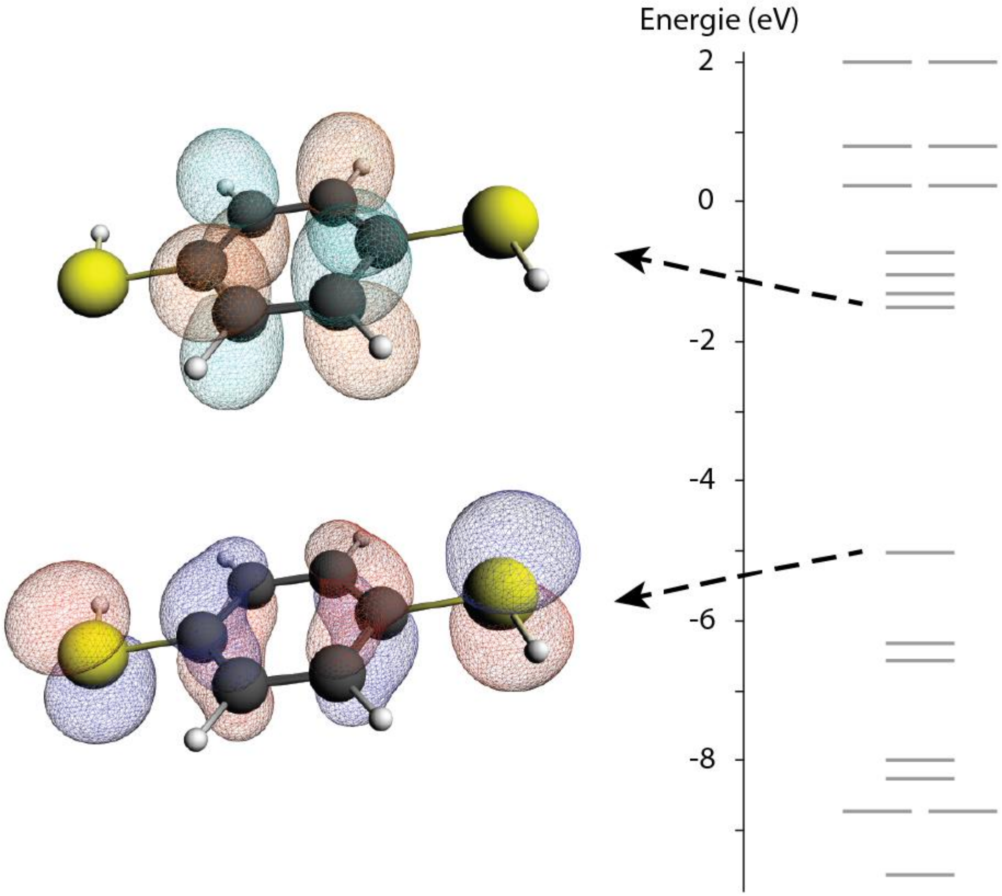
DFT Results

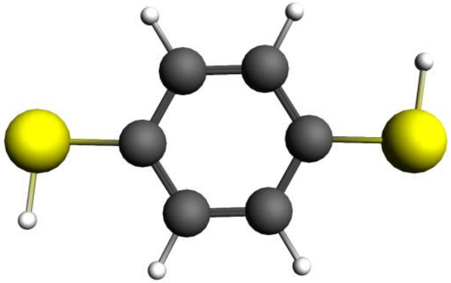
- DFT provides the energy of the molecular orbitals
- DFT provides the wave-functions of the molecular orbitals



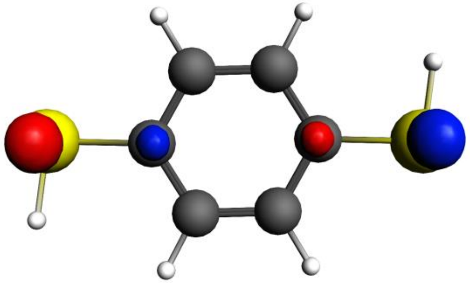
Molecular orbitals

- # electrons per cubic ångström
- Positive and negative part of the wave function

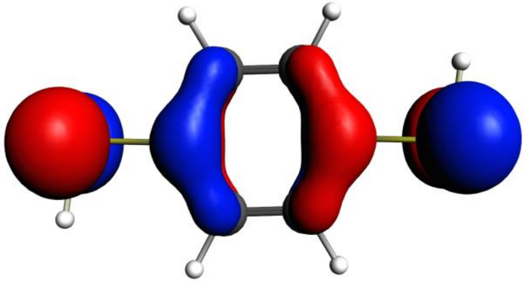
0.5



0.1



0.05



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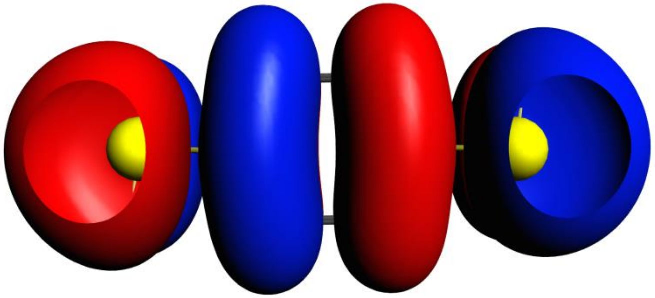
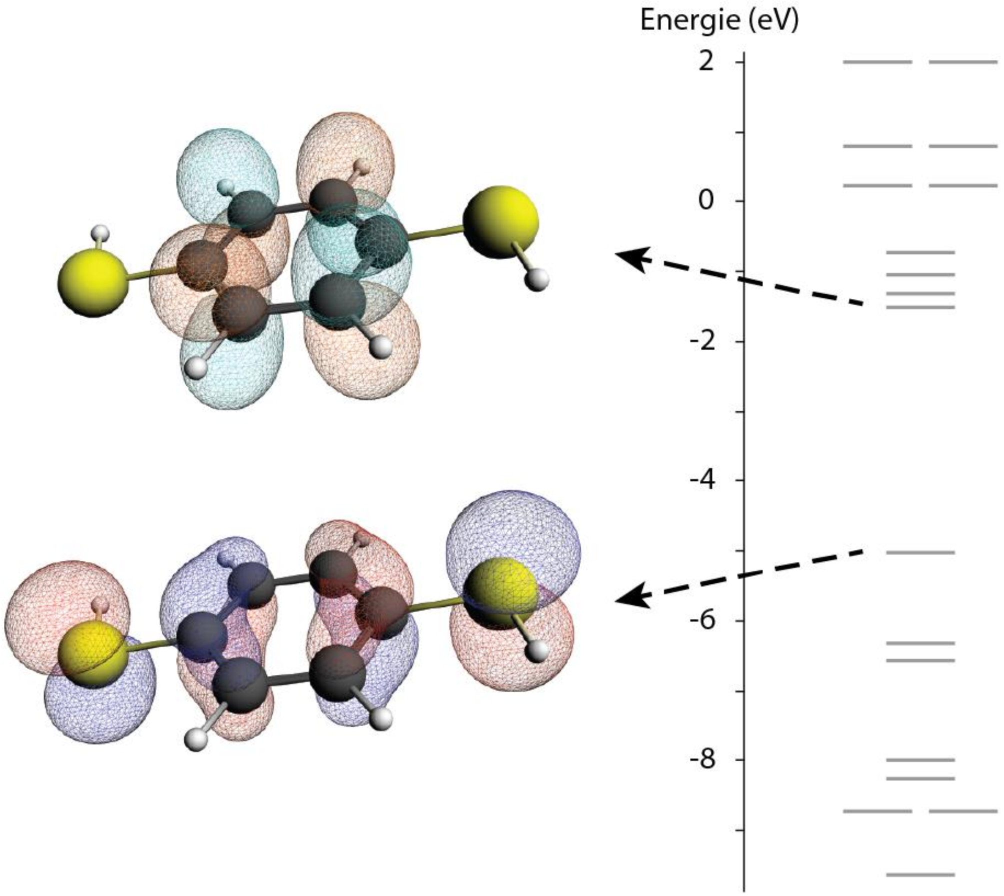


DFT Results

- DFT provides the energy of the molecular orbitals
- DFT provides the wave-functions of the molecular orbitals
- Molecular Orbitals are linear combinations of basis-set functions

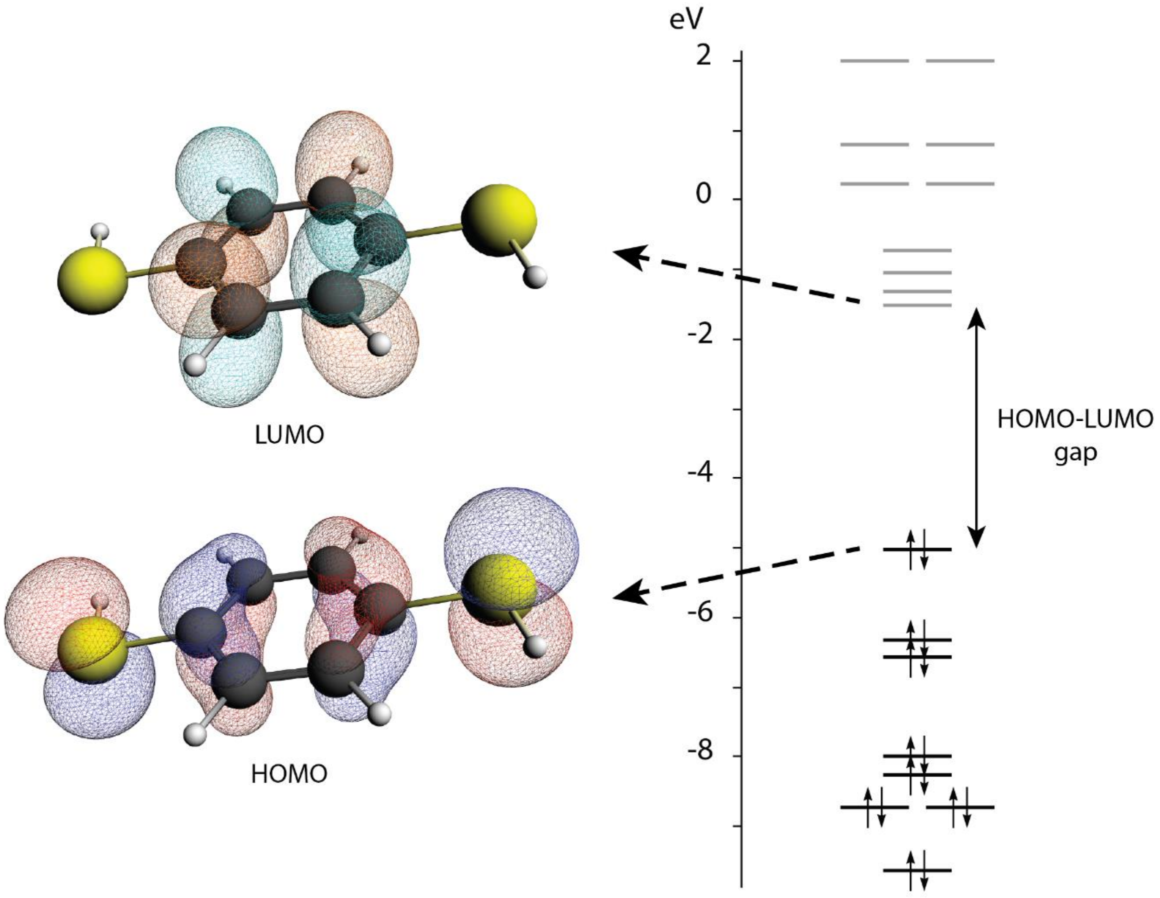


DFT Results

- Orbitals are populated from the bottom (Aufbau principle)

- Each orbital can be occupied by at most two electrons (Pauli principle)

- HOMO/LUMO



Summary DFT

- Density functional theory is an **exact reformulation** of many-body quantum mechanics in terms of the density rather than the wave function

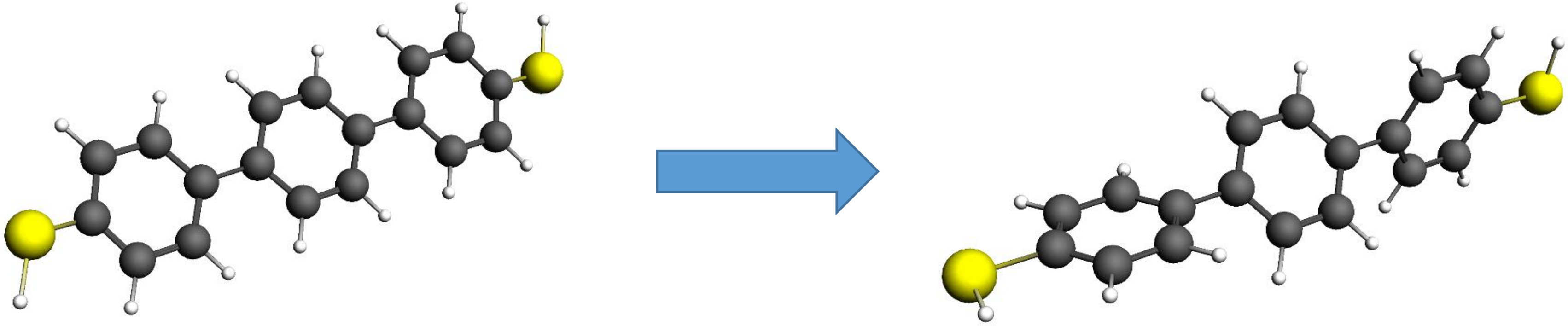
- DFT provides electron density and hence the wave function

- XC functional unknown : electron exchange and correlation effects are approximated

- The result is as good as the functional/basis-set you are using

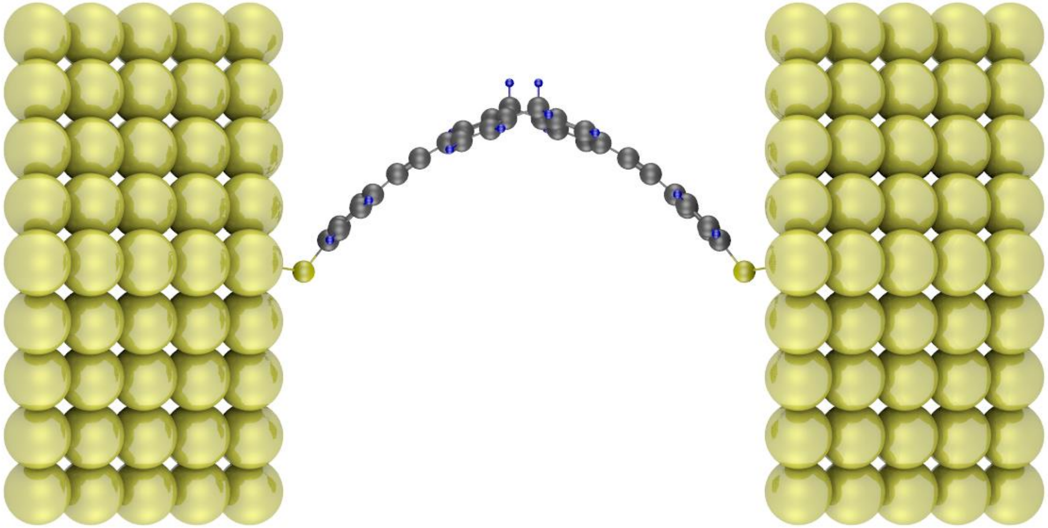
Geometry optimization

- Look for lowest energy configuration
- Based on energy gradient



Geometry constraints

- Fix specific atoms or blocks of atoms
- Fix specific bond length, angles etc…



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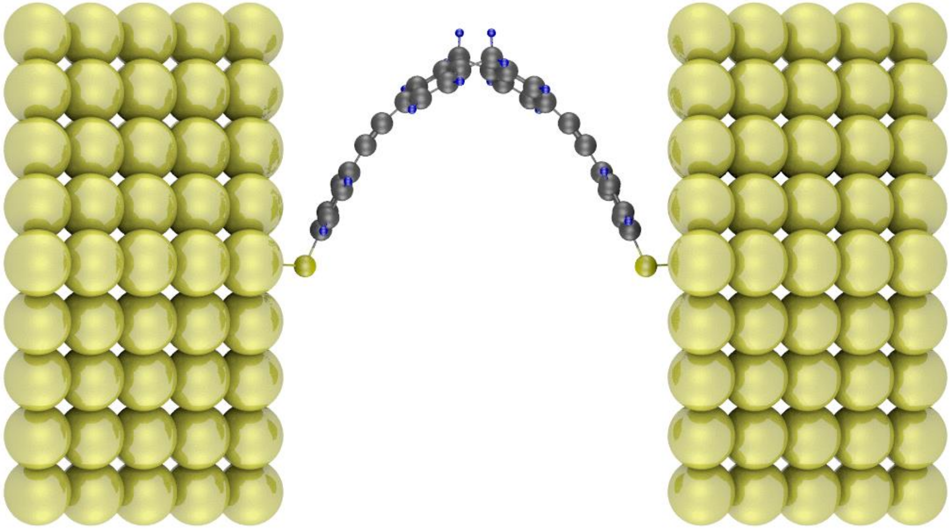
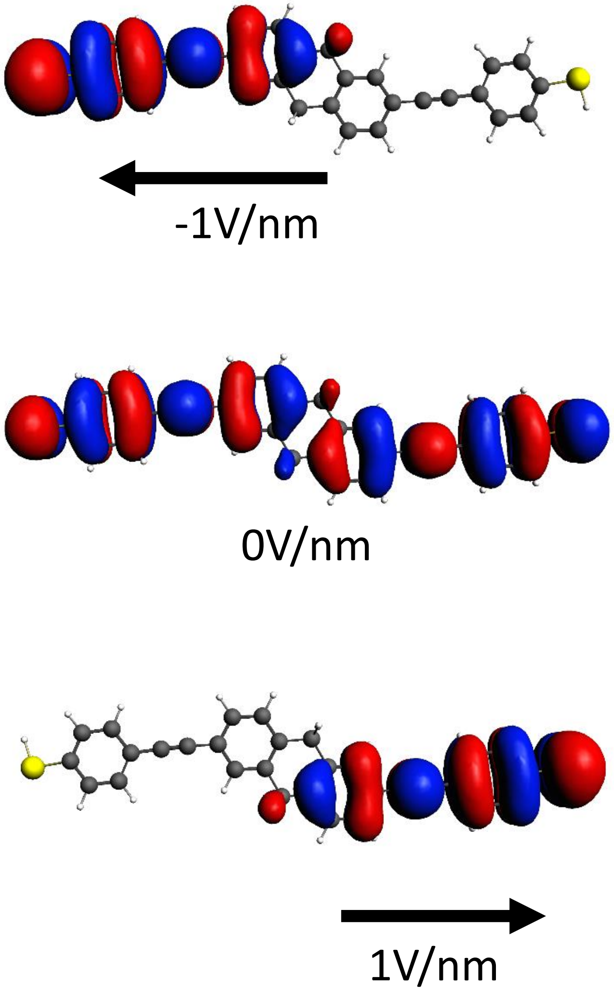


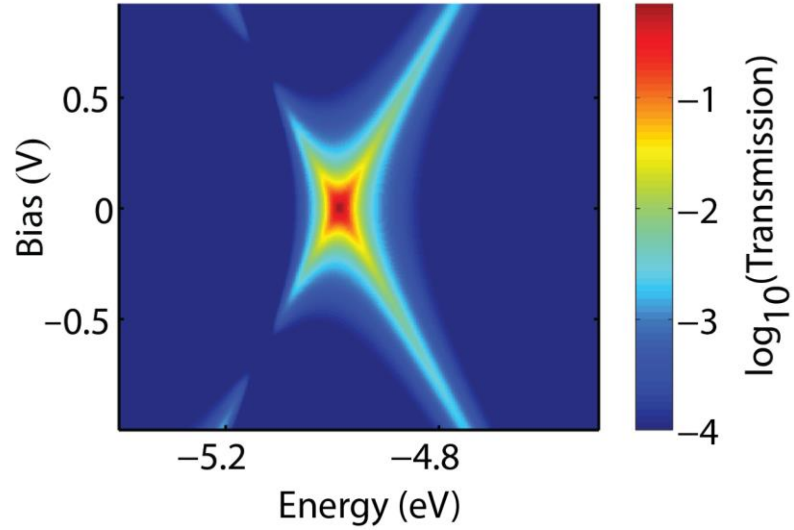
Electric fields

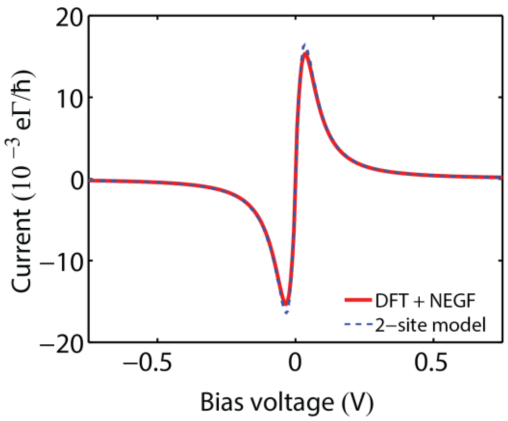
- An electric field can be added



Electric fields

- An electric field can be added
- Bias dependence transmission
- Useful to calculate IVs



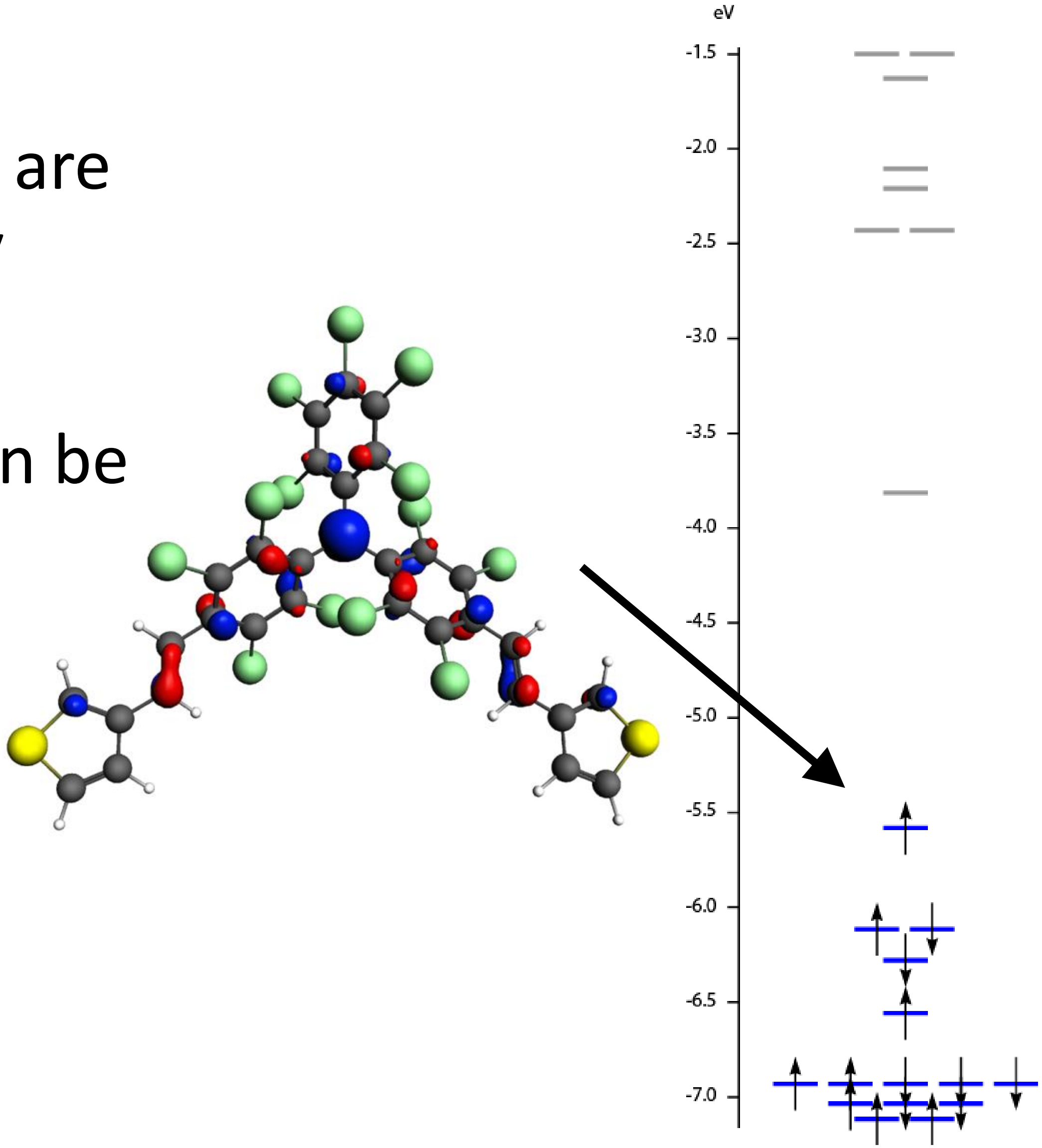


Spin resolved calculations

- Spin up and down are treated separately

- Spin unbalance can be added

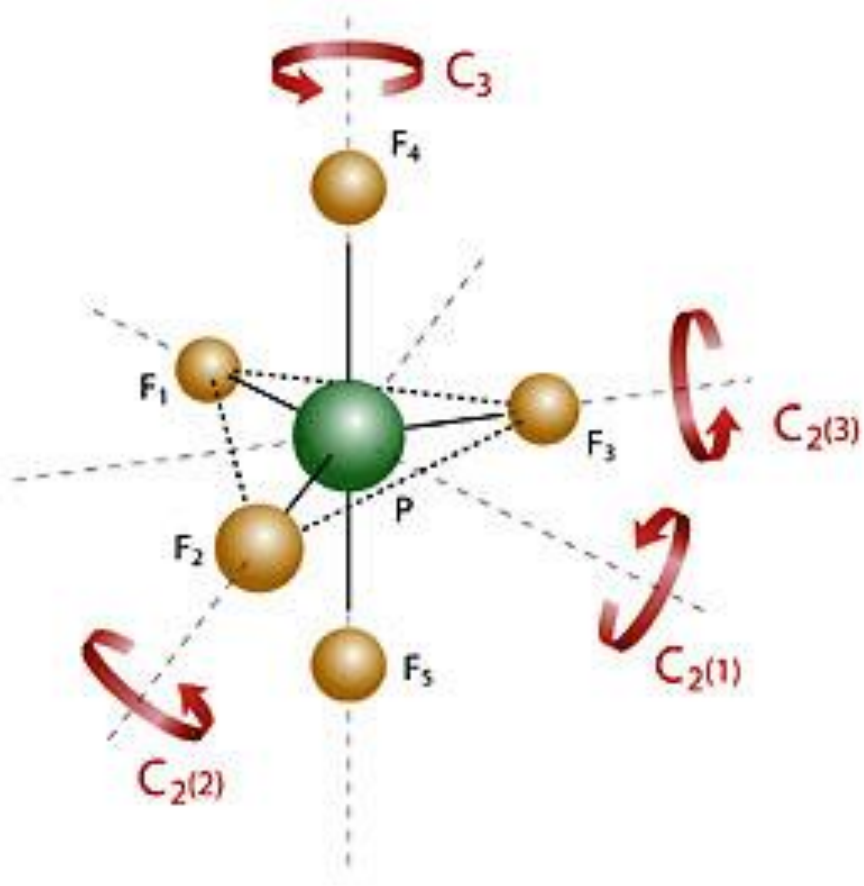
- Add charge to molecule



SCF tricks/speed-up

- Molecular symmetry
- Fragments
- Frozen core
- Electron smearing

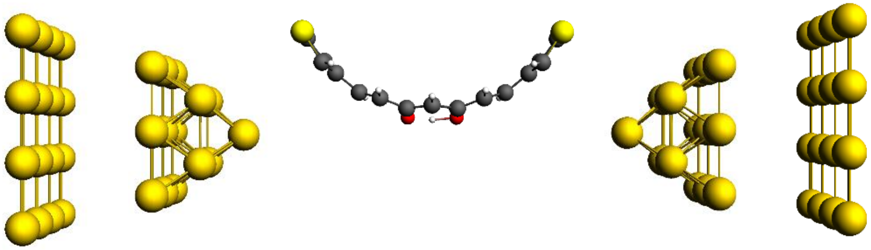
SCF tricks/speed-up - Symmetry



- Enforce symmetry in geometry optimization (reflection, rotation,…)
- Easier to converge
- Speeds up the calculations

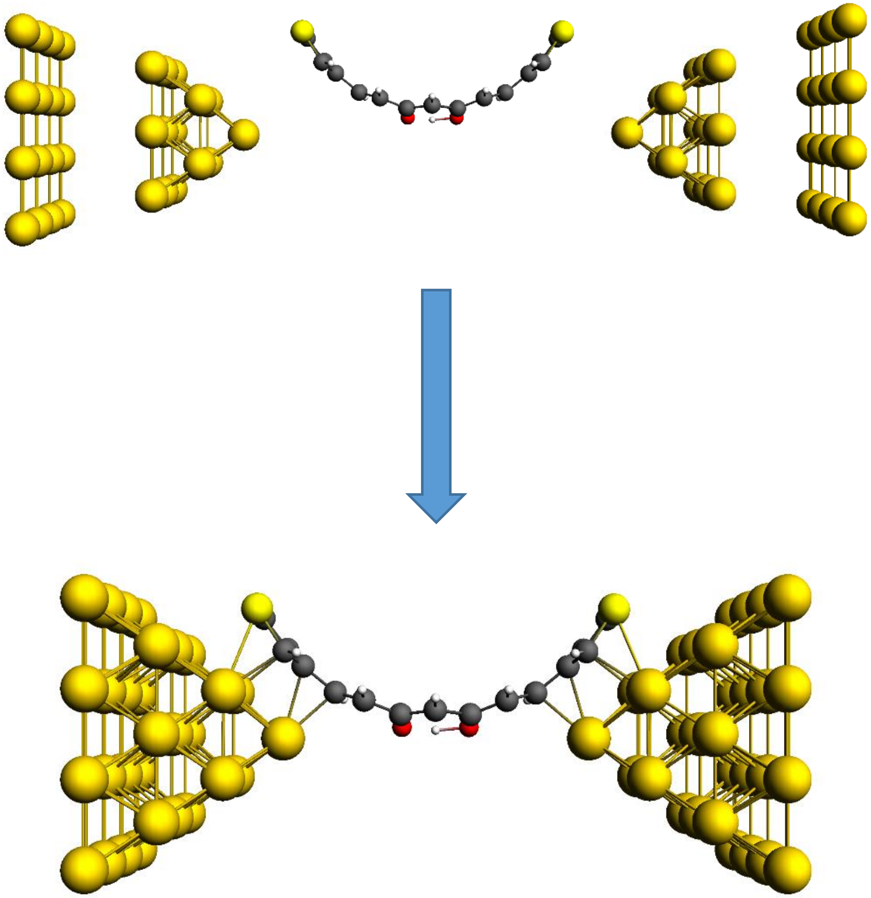
SCF tricks/speed-up – Fragments

- Fragments are first converged separately
- Provides better guess for initial density



SCF tricks/speed-up – Fragments

- Fragments are first converged separately
- Provides better guess for initial density
- Allows for convergence which otherwise would be difficult/impossible
- Speeds up convergence



SCF tricks/speed-up – Frozen core

- Deep-core atomic orbitals change very little upon bond formation

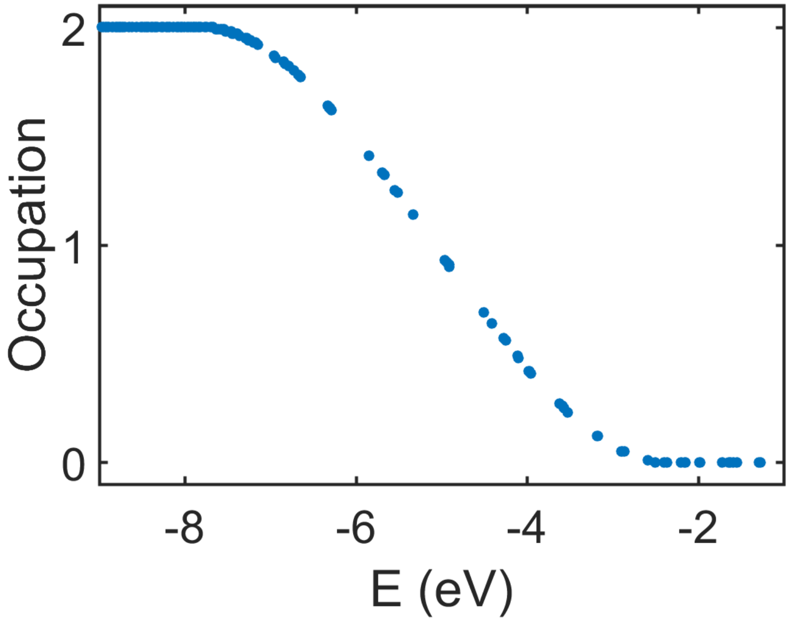
- DFT can ‘freeze’ the core electrons of atoms

SCF tricks/speed-up – Frozen core

- Deep-core atomic orbitals change very little upon bond formation
- DFT can ‘freeze’ the core electrons of atoms
- Reduces the size of the variational basis set and speeds up calculations
- Core electrons taken into account when calculating energy

SCF tricks/speed-up – Smearing

- Electrons are ‘smeared out’, allowing for partial occupation of orbitals



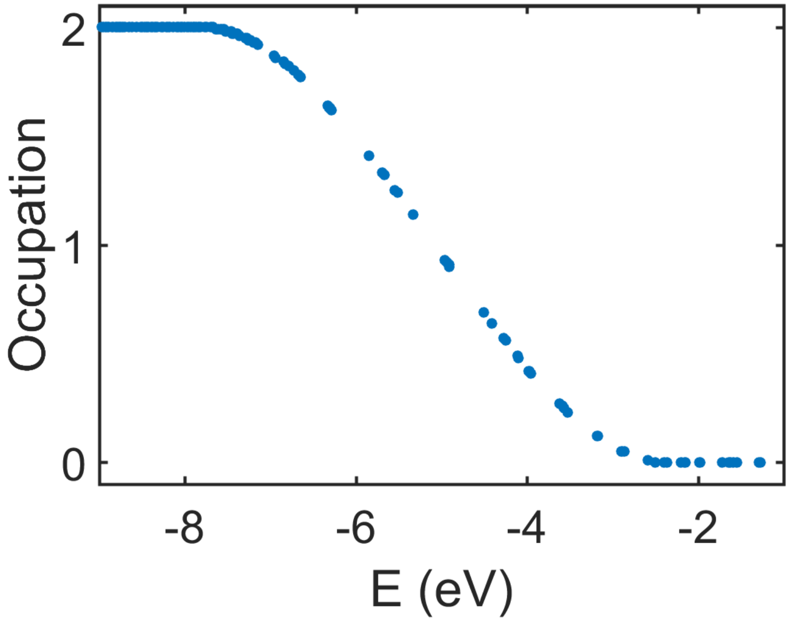
SCF tricks/speed-up – Smearing

- Electrons are ‘smeared out’, allowing for partial occupation of orbitals

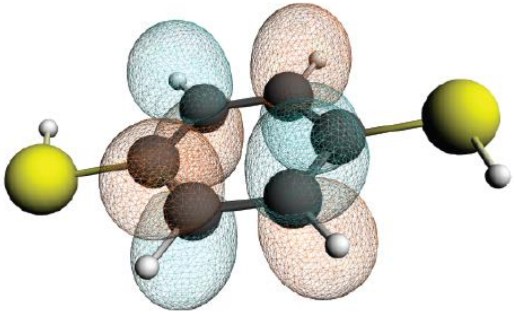
- Allows for convergence which otherwise would be difficult/impossible

- Speeds-up convergence

- Especially useful for clusters of metals with many closely located orbitals



Overview



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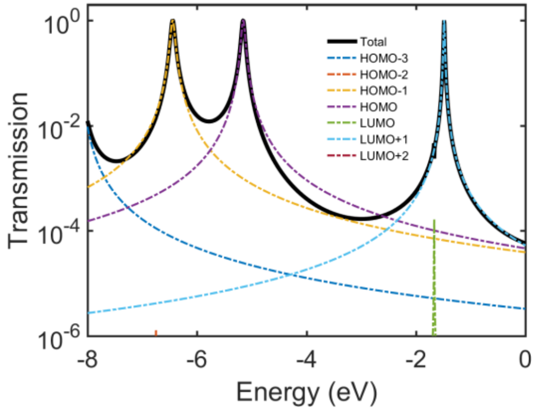
- Non-equilibrium Green's function (NEGF)



NEGF

For charge transport, time dependent Schrödinger equation needs to be solved

$$i\hbar\frac{\partial}{\partial t}\Psi(\mathbf{r},t) = \hat{H}\Psi(\mathbf{r},t)$$

NEGF

For charge transport, time dependent Schrödinger equation needs to be solved

$$i\hbar\frac{\partial}{\partial t}\Psi(\mathbf{r},t) = \hat{H}\Psi(\mathbf{r},t)$$

After a lot of math, the transmission is given by

$$T(\epsilon) = \mathrm{Tr}\left\{\mathbf{\Gamma}_L(\epsilon)\boldsymbol{G}^r(\epsilon)\mathbf{\Gamma}_R(\epsilon)\boldsymbol{G}^a(\epsilon)\right\}$$

G^r is the retarded Green's function

$$\boldsymbol{G}^r(\epsilon) = \left[\epsilon\boldsymbol{S} - \boldsymbol{H} - \mathbf{\Sigma}_L^r(\epsilon) - \mathbf{\Sigma}_R^r(\epsilon)\right]^{-1}$$

NEGF

$$\boldsymbol{G}^r(\epsilon) = \left[\epsilon \boldsymbol{S} - \boldsymbol{H} - \boldsymbol{\Sigma}_L^r(\epsilon) - \boldsymbol{\Sigma}_R^r(\epsilon)\right]^{-1}$$

ε → Energy incoming electron

S → Overlap matrix (DFT)

Overlap of basis-set functions (atomic orbitals).

If orthonormal basis, S is identity matrix

H → Fock matrix (DFT)

Eigenvalues: Orbital energies

Eigenvectors: Orbital shape, linear combination atomic orbitals

Σ → Self energy matrix (DFT/arbitrary)

$$\boldsymbol{\Sigma}_{L,R}^r(\epsilon) = \boldsymbol{\Lambda}_{L,R}(\epsilon) - \frac{\mathrm{i}}{2}\boldsymbol{\Gamma}_{L,R}(\epsilon)$$

Wide-band limit

Wide-band limit (WBL) assumes self-energy is energy independent

$$\boldsymbol{\Sigma}^{r}_{L,R} = \boldsymbol{\Lambda}_{L,R} - \frac{\mathrm{i}}{2}\boldsymbol{\Gamma}_{L,R}$$

and neglects the real part

$$\boldsymbol{\Sigma}^{r}_{L,R} = -\frac{\mathrm{i}}{2}\boldsymbol{\Gamma}_{L,R}$$

Wide-band limit

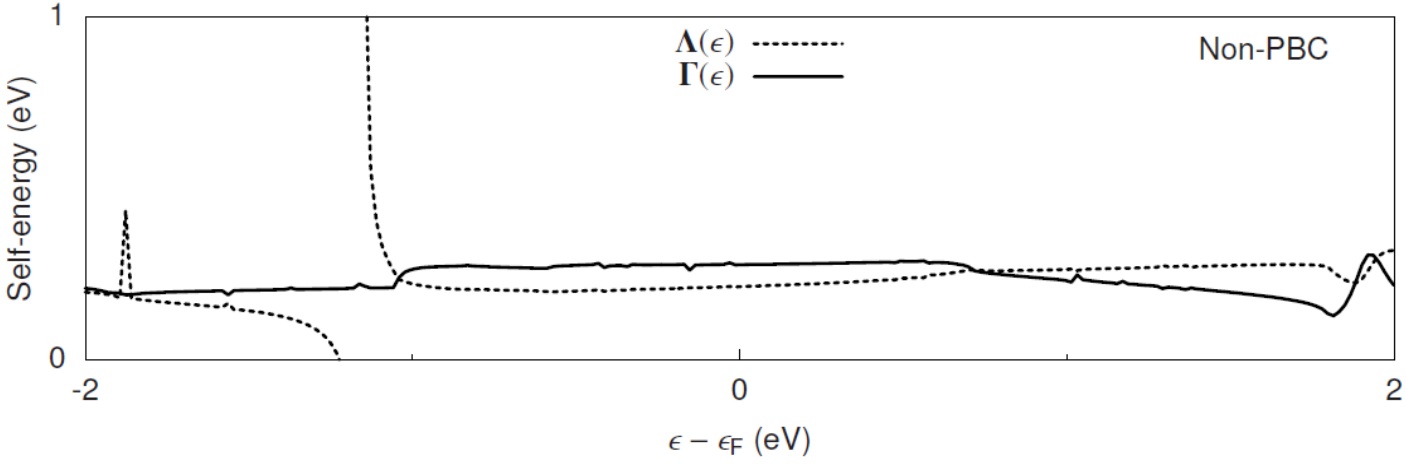
Wide-band limit (WBL) assumes self-energy is energy independent

$$\Sigma^{r}_{L,R} = \Lambda_{L,R} - \frac{i}{2}\Gamma_{L,R}$$

and neglects the real part

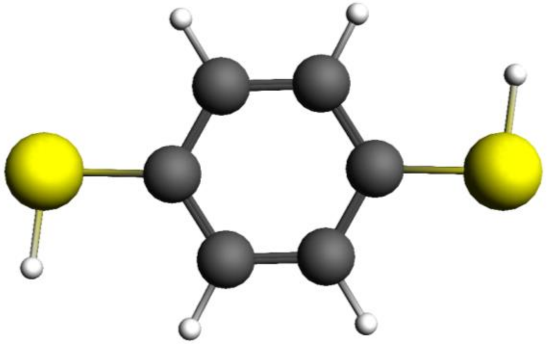
$$\Sigma^{r}_{L,R} = -\frac{i}{2}\Gamma_{L,R}$$

For gold this is a not-so-crazy assumption



Gas phase transmission

1. Take fock matrix from DFT (H)



2. Take overlap matrix from DFT (S)

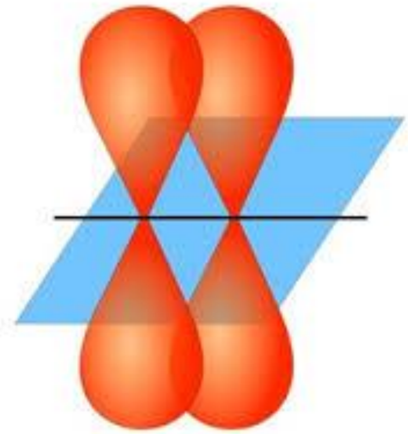
3. Chose were to inject charge and construct $\Gamma_{R,L}$ accordingly.

4. Compute transmission

$$T(\epsilon) = \mathrm{Tr}\left\{\Gamma_L(\epsilon) G^r(\epsilon) \Gamma_R(\epsilon) G^a(\epsilon)\right\}$$

Neglects all electrodes/molecule interactions!

Gas phase transmission



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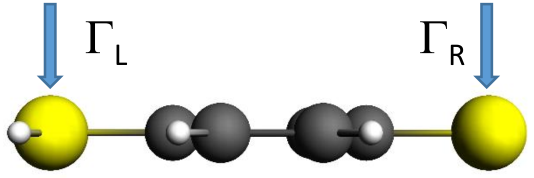

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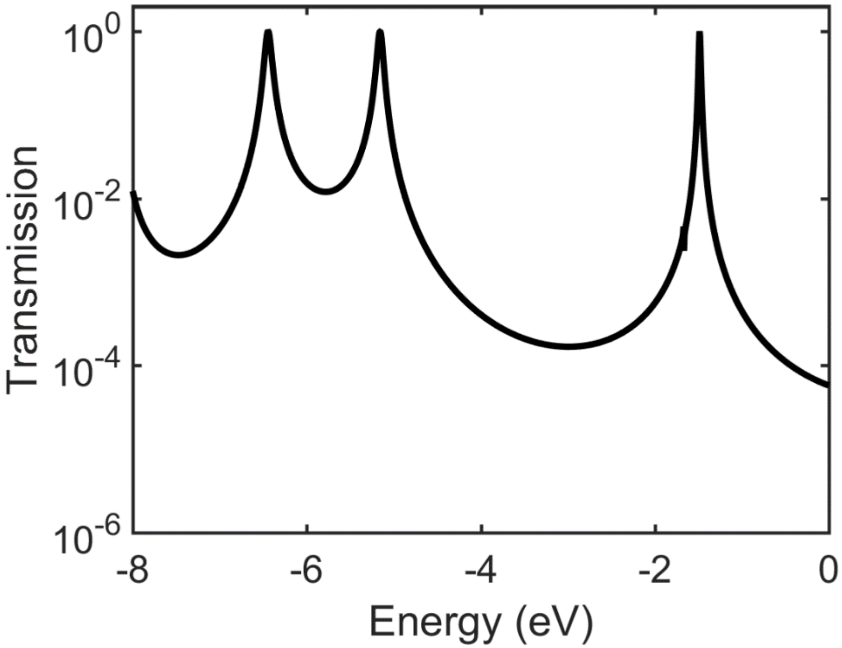
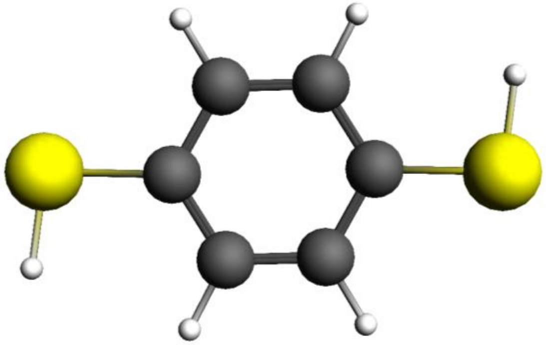
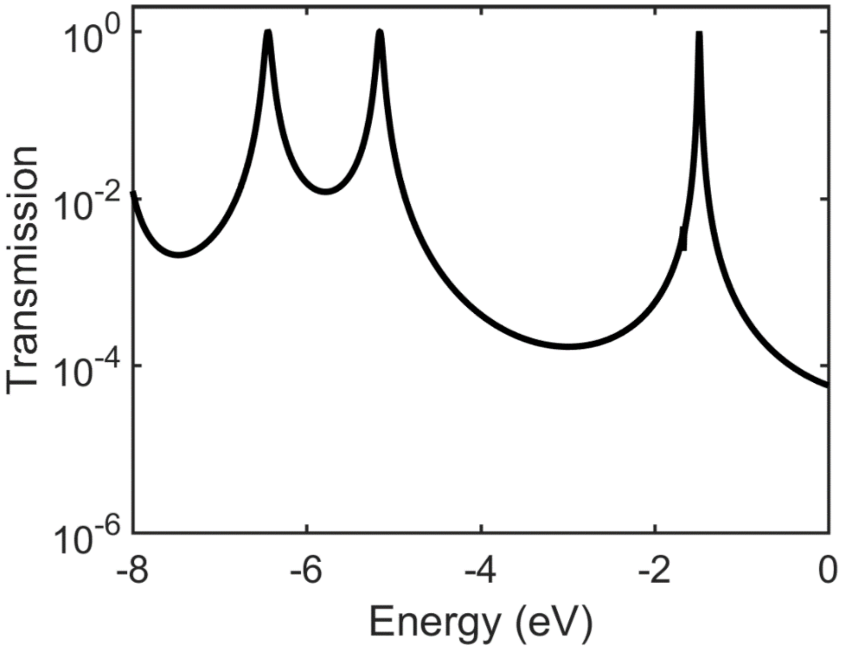
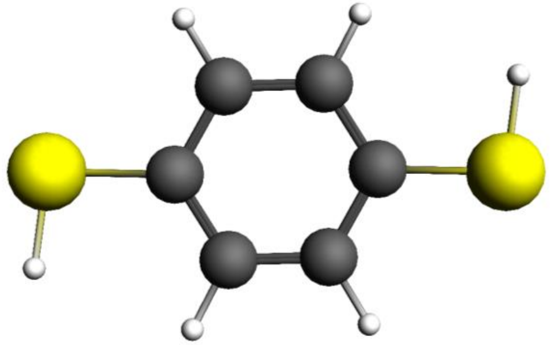
Gas phase transmission

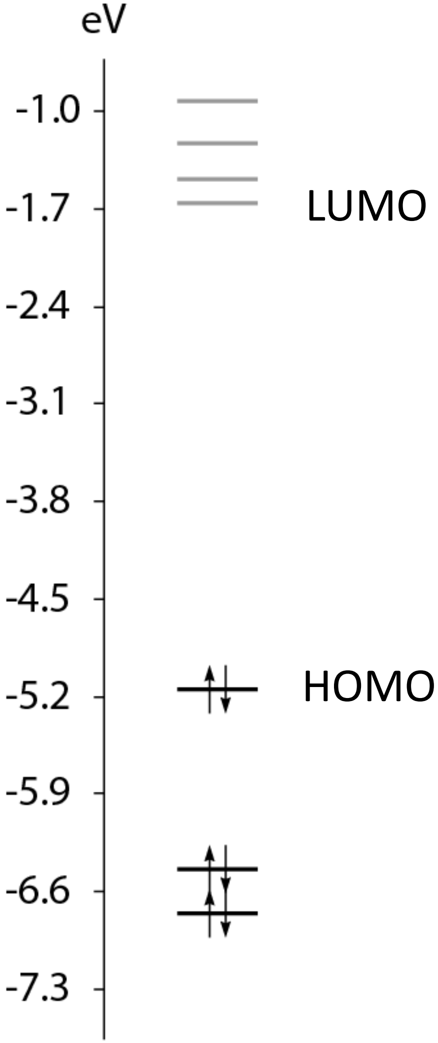




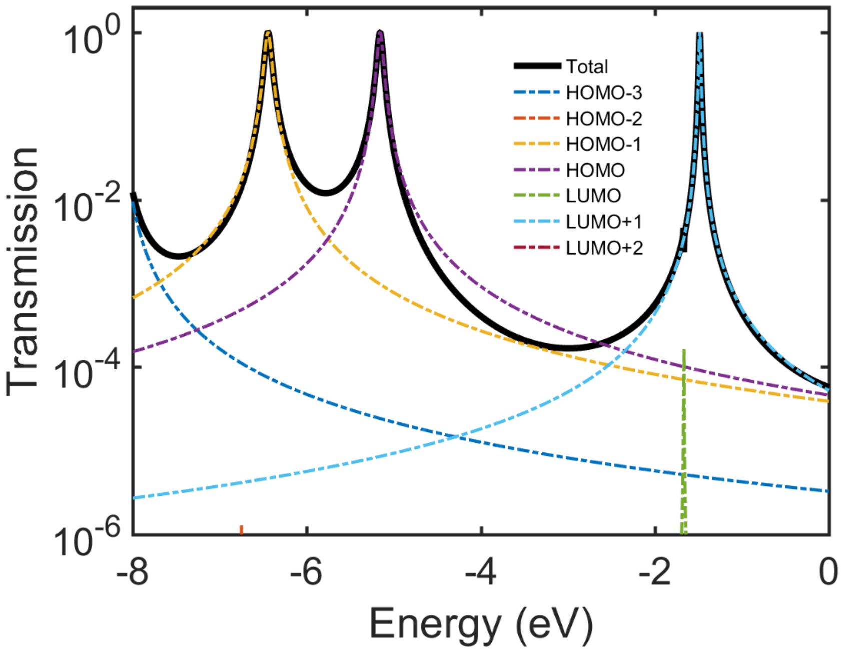
Gas phase transmission

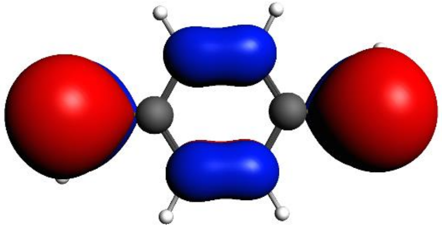




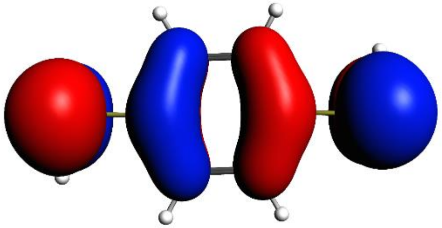


Orbital decomposition - amplitude

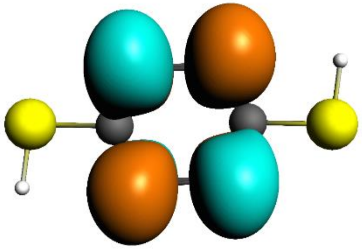




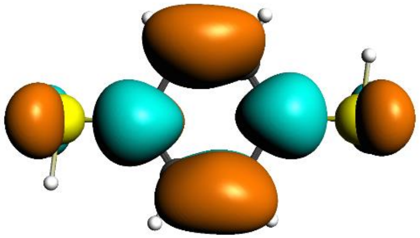
HOMO-1



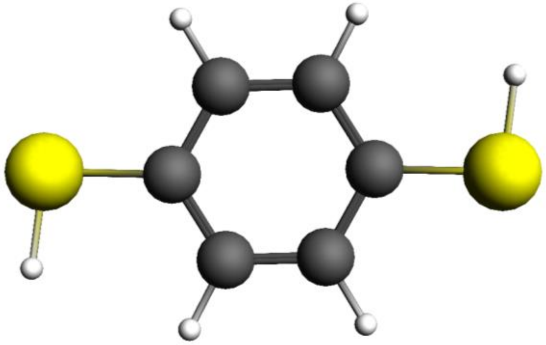
HOMO



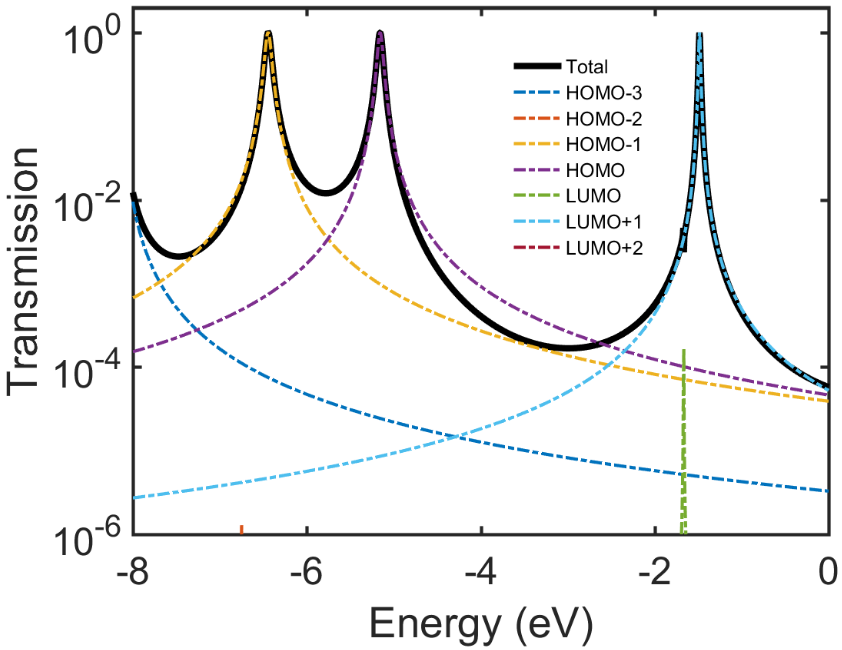
LUMO

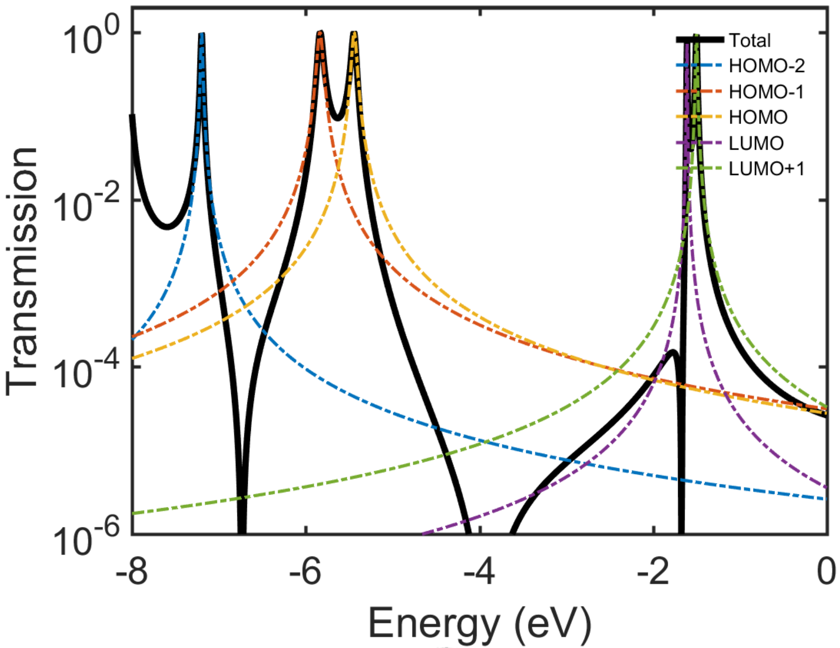


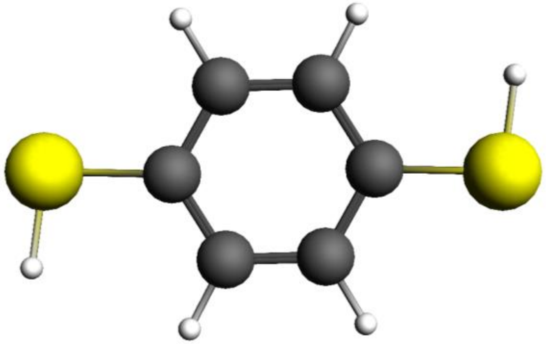
LUMO+1

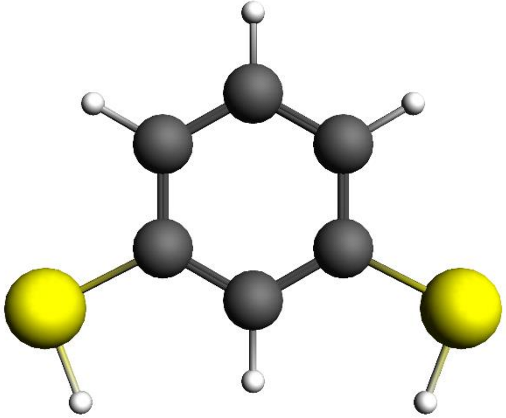


Orbital decomposition - amplitude

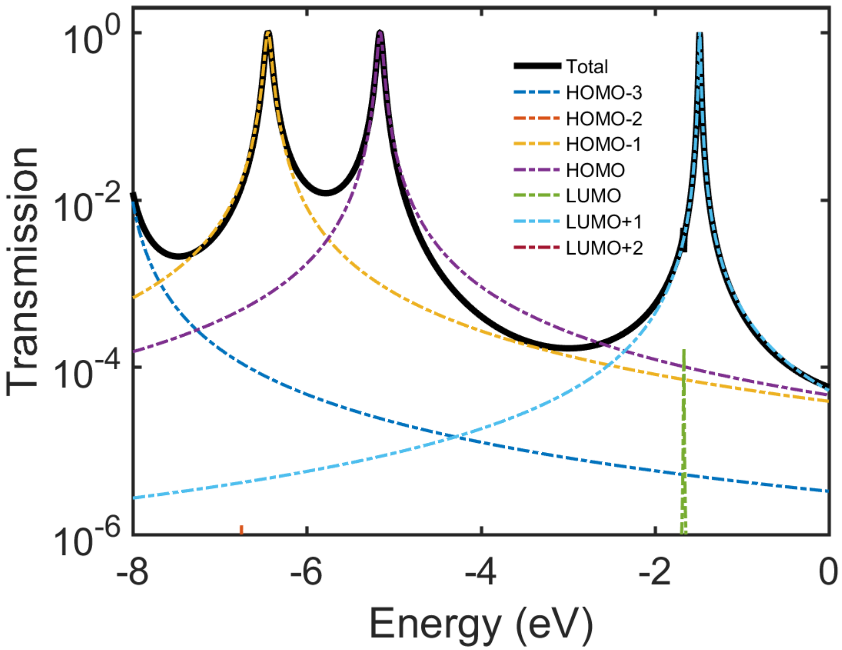


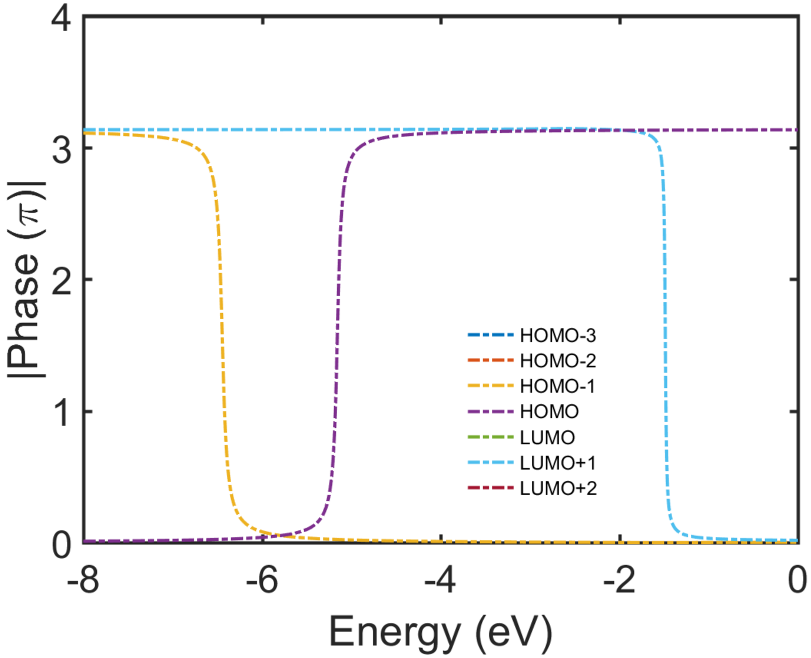


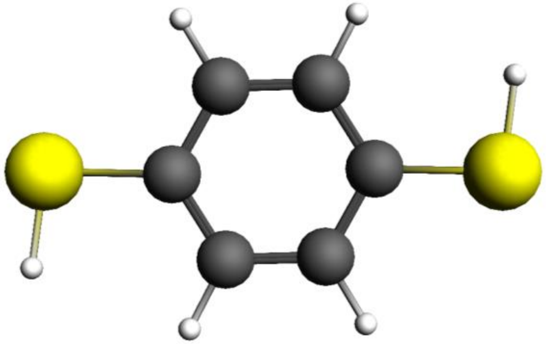




Orbital decomposition - phase



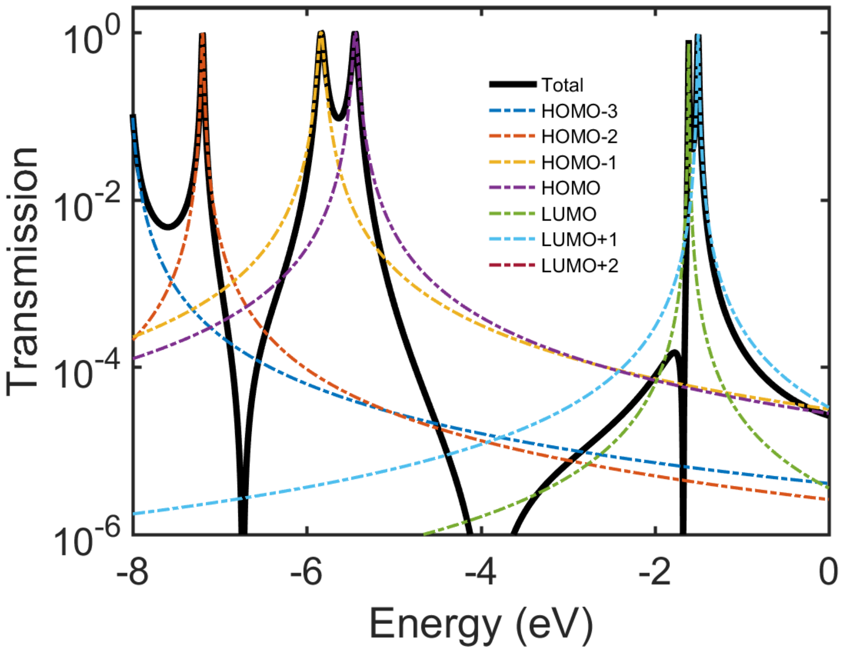


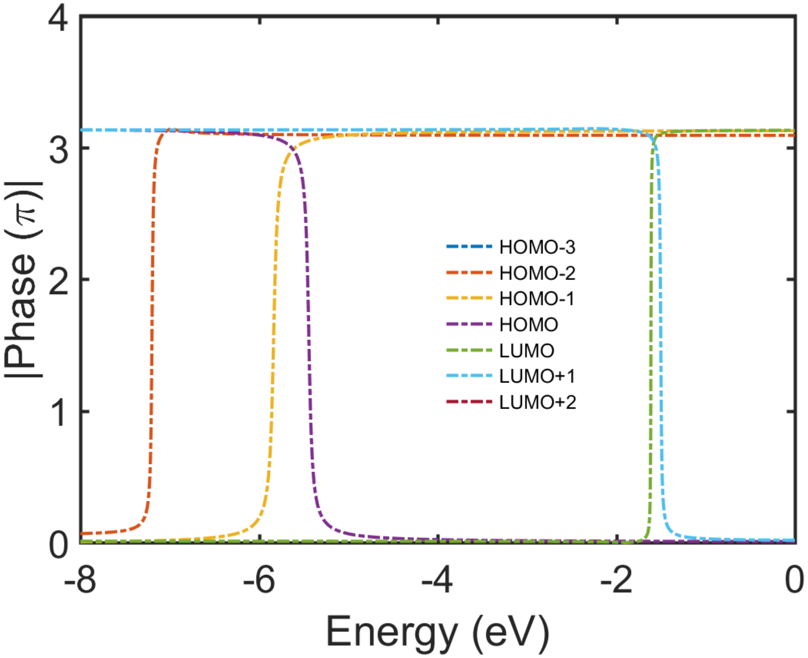


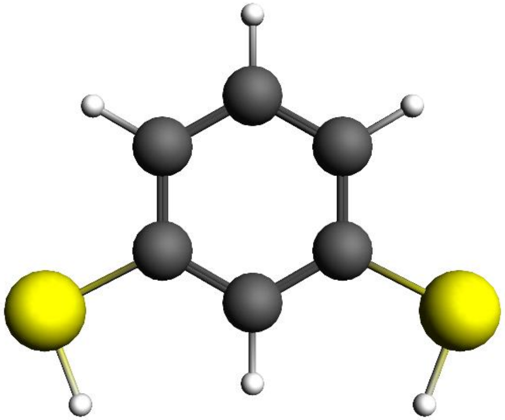
Phase is angle between real and complex part of the transmission

π-phase shift at energy of corresponding orbital

Orbital decomposition - phase





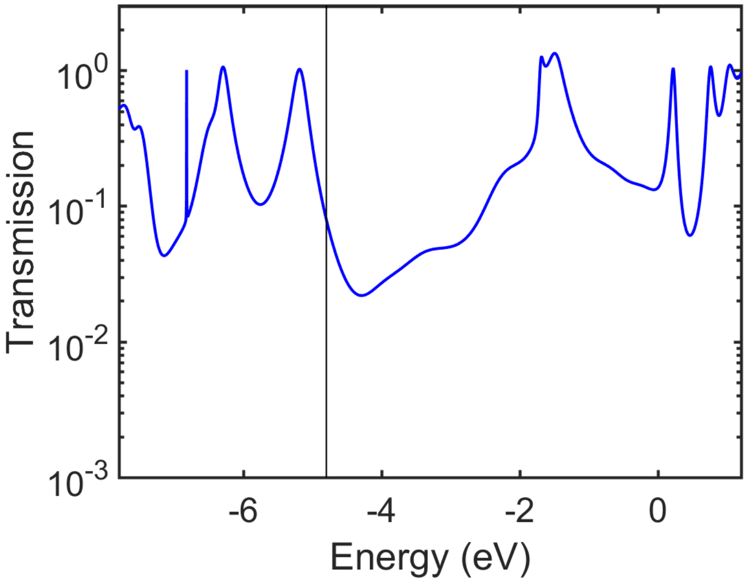


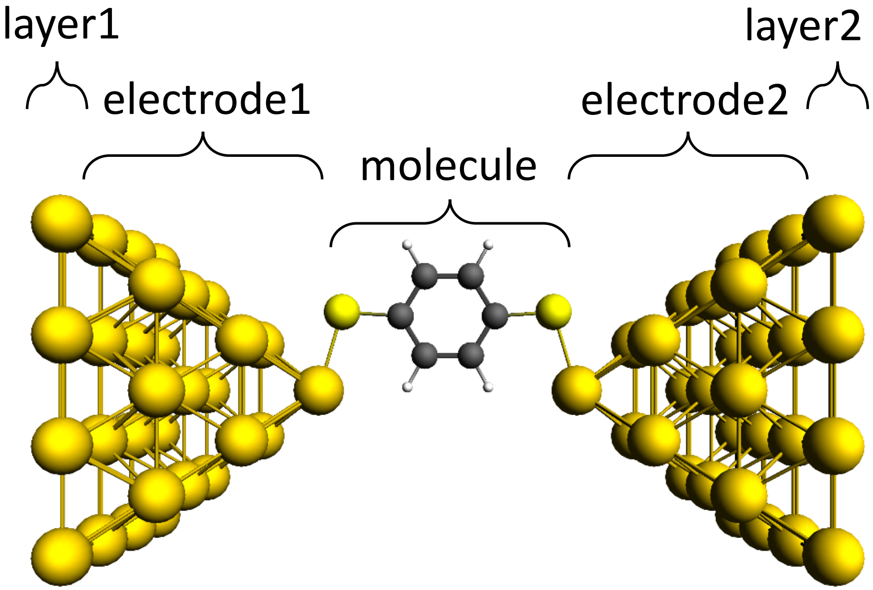
Phase is angle between real and complex part of the transmission

Destructive interference occurs when amplitude is the same, but π-phase shift

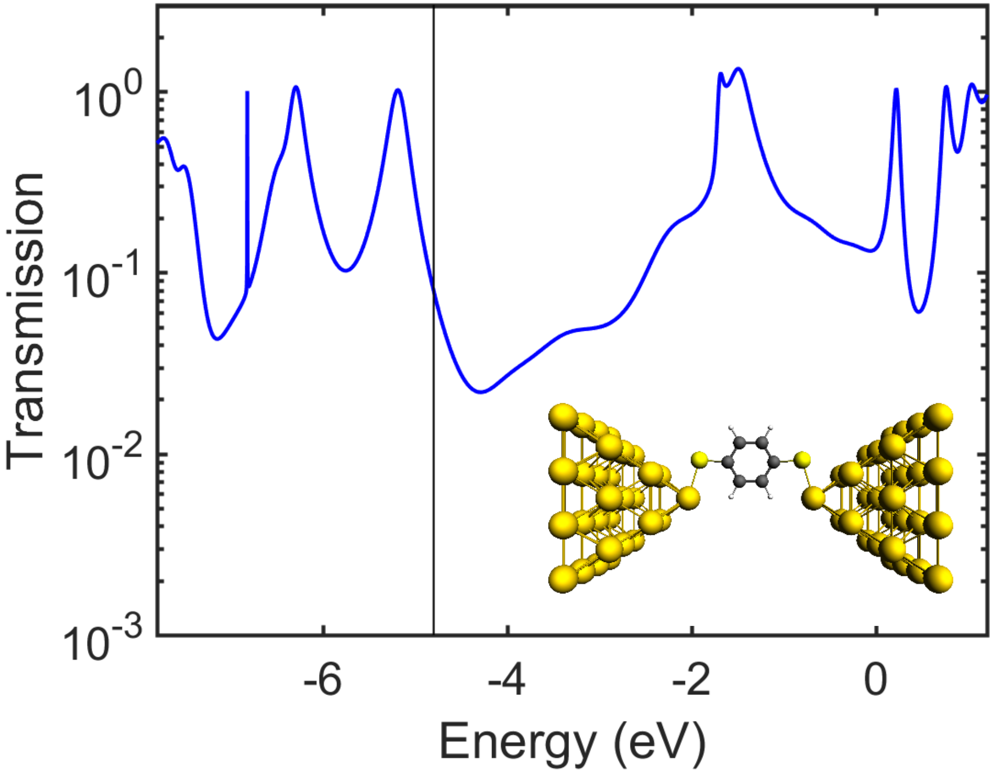
Transport with gold electrodes

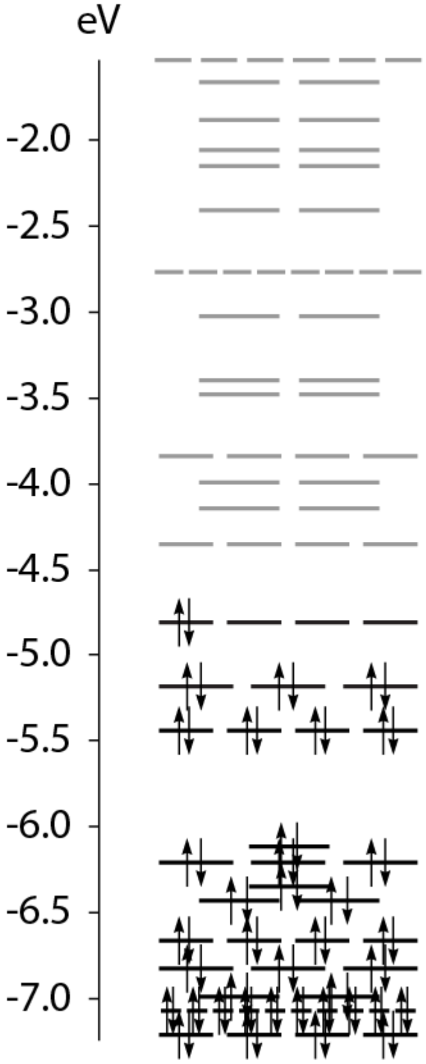
- Couple to atomic orbitals of gold of outermost layer instead of S atoms.





Transport with gold electrodes

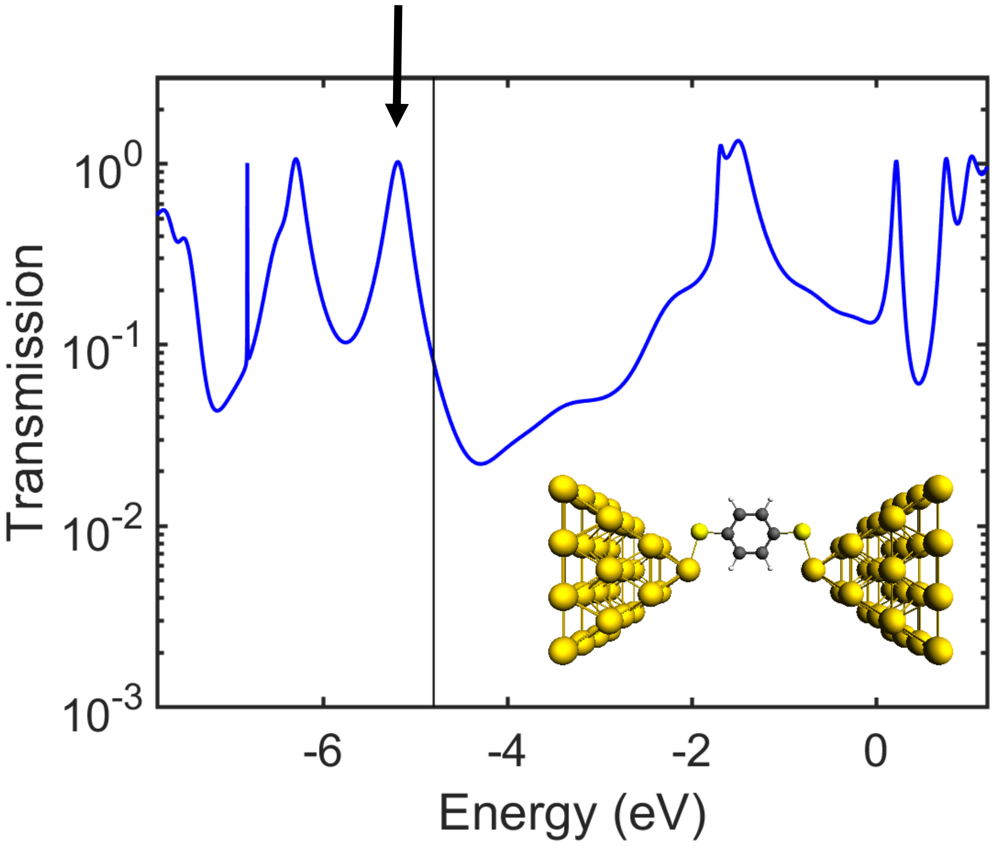




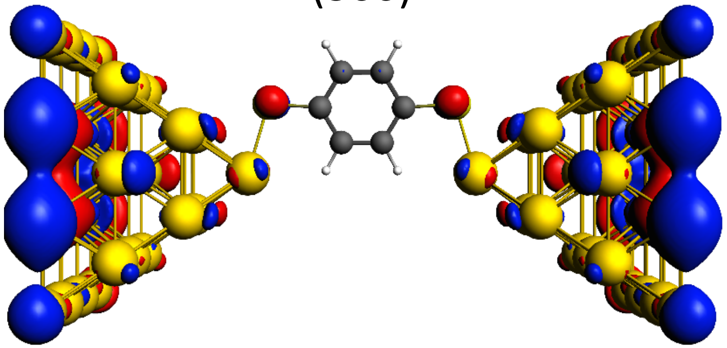
With so many orbitals, how to identify relevant ones?

Transport with gold electrodes

‘true’ HOMO



junction HOMO
(366)



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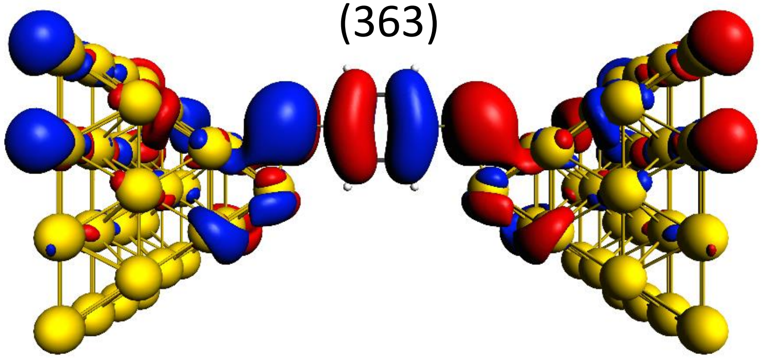
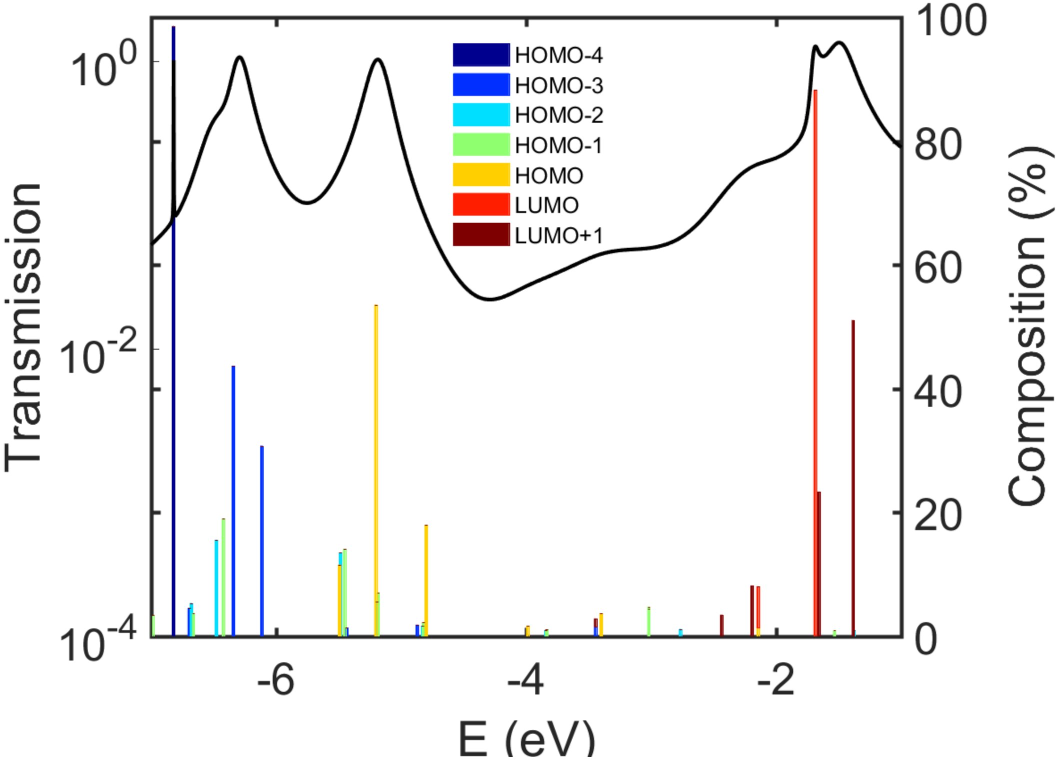
(363)

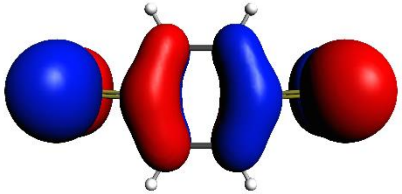


Which ‘gas phase’ orbital is responsible for transport?

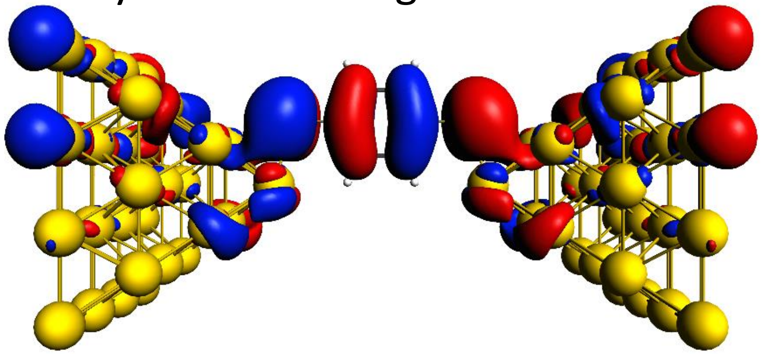
Orbital projections



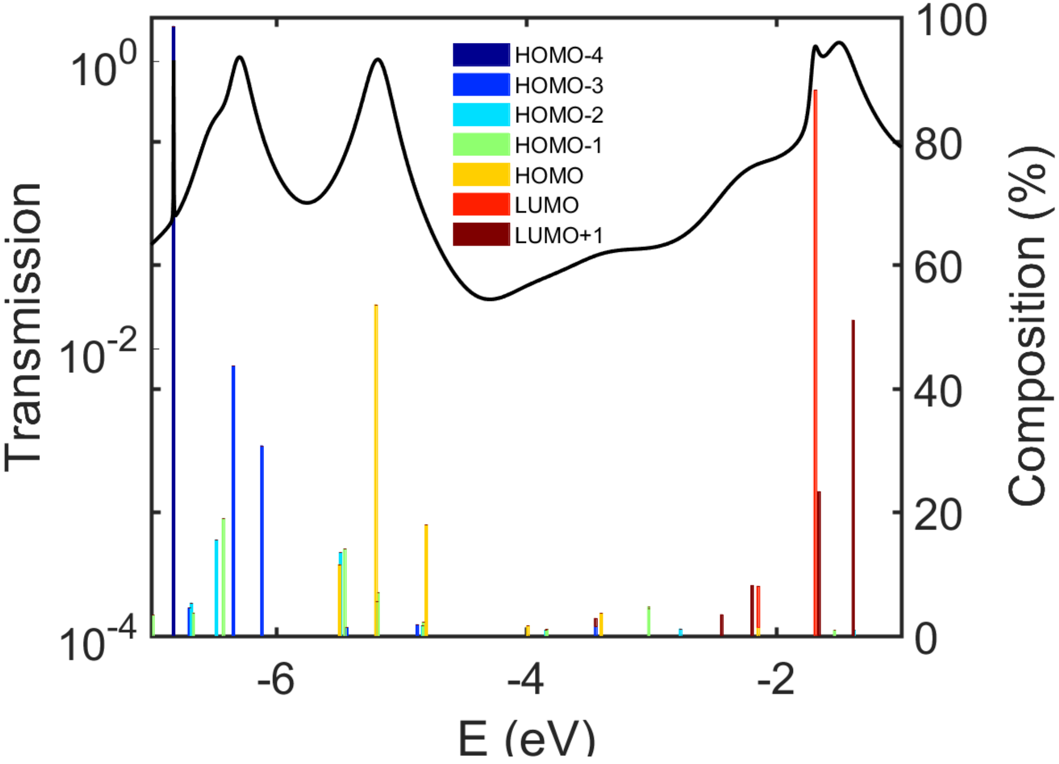
Gas phase HOMO



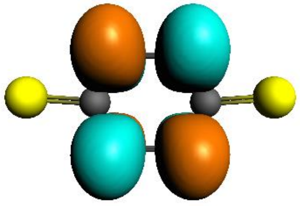
hybridized → high conduction



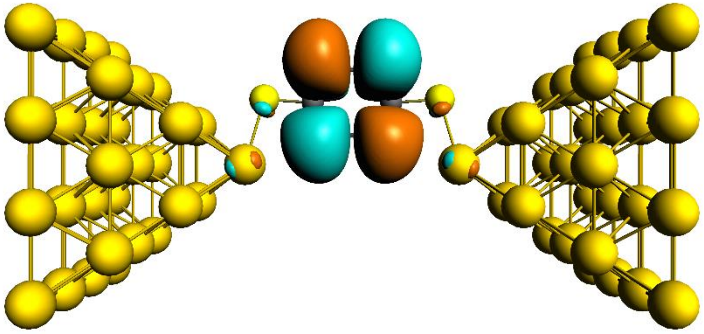
Orbital projections



Gas phase LUMO

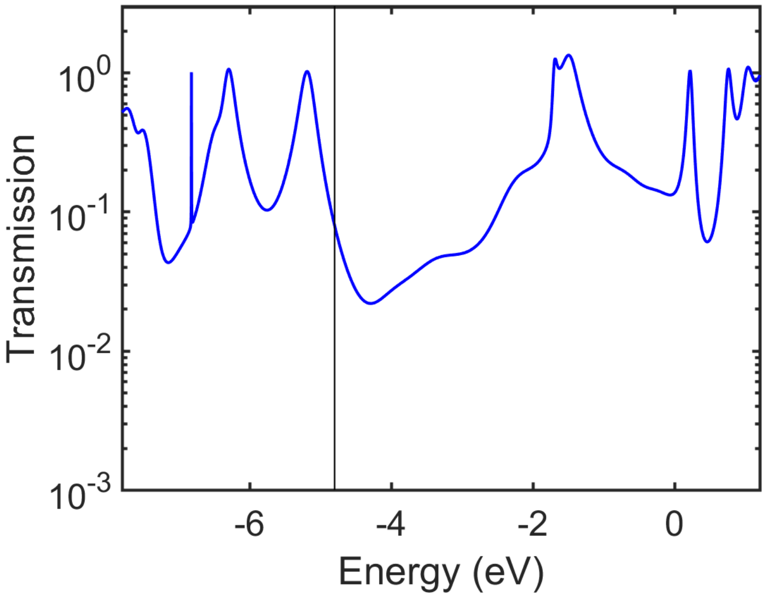


not hybridized → poor conduction



How does this compare to experiments?

Bandgap underestimated, conductance overestimated

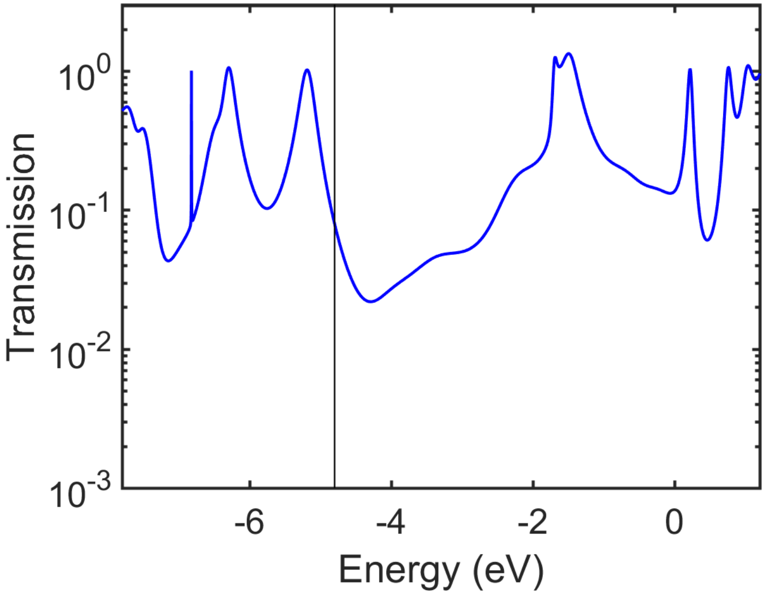


How does this compare to experiments?

Bandgap underestimated, conductance overestimated

1. DFT does not properly account for addition/removal of charge

2. Formation of image-charges in the electrodes upon addition/removal of charge not taken into account

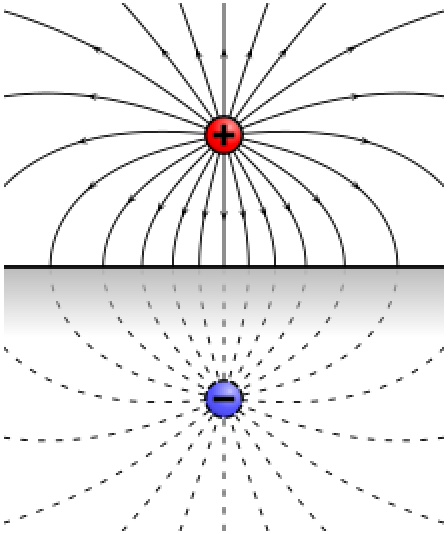


DFT + Σ

- Correct HOMO and LUMO by performing a **calculation for ±1e**

  → increases bandgap a lot

DFT + Σ



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- Correct for **image-charge formation** in electrodes (classical electrostatics)

  → reduces bandgap a bit

DFT + Σ

- Correct HOMO and LUMO by performing a **calculation for ±1e**

  → increases bandgap a lot

- Correct for **image-charge formation** in electrodes (classical electrostatics)

  → reduces bandgap a bit

- Shift for (un)occupied levels implemented as **scissor operator**

- Significantly improves agreement with experimental conductance values