

BCCMS Seminar

# Electronic coarse-graining of (organic) semiconductors: methods and applications

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## Acknowledgments

Sergei Tretiak (LANL)



MAX PLANCK INSTITUTE  
FOR POLYMER RESEARCH



# Intro 1/4: What is organic semiconductor

1. **Organic** – built from C with terminal H, possibly with isovalent substitutions (N for CH, O/S for CH<sub>2</sub>, F/Cl for H)
2.  **$\pi$ -conjugated** – only  $\pi$ -electrons on frontier orbitals

①	②						
H							
Li	Be						
Na	Mg						
K	Ca						
Rb	Sr						
Cs	Ba						
Fr	Ra						
La-Yb	Lu Ta Re Ir Au Hf W Os Pt Hg						
Ac-No							

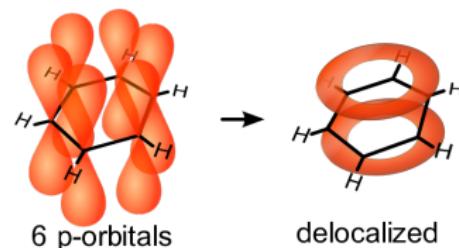
*valence shells*

$\Delta\epsilon$

*d-shell*

*f-shell*

*strong relativistic effects*



$$t_{sp2} = 3.26 \frac{\hbar^2}{md^2} \gg t_{pp\pi} = 0.63 \frac{\hbar^2}{md^2}$$

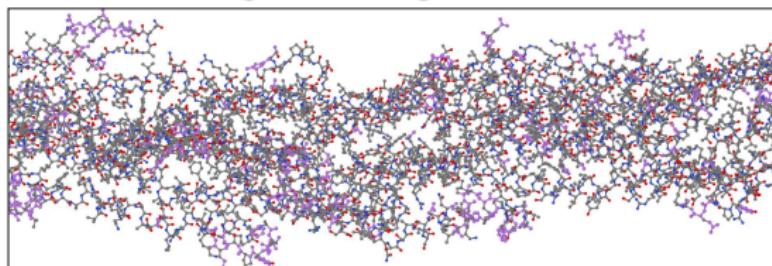
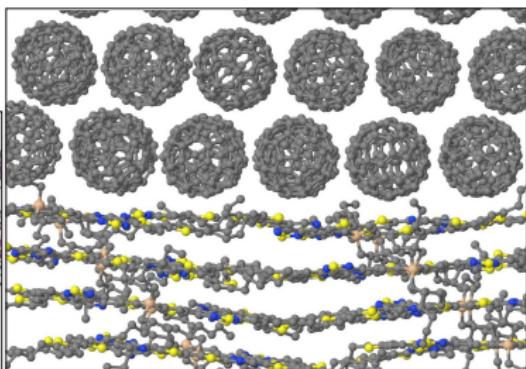
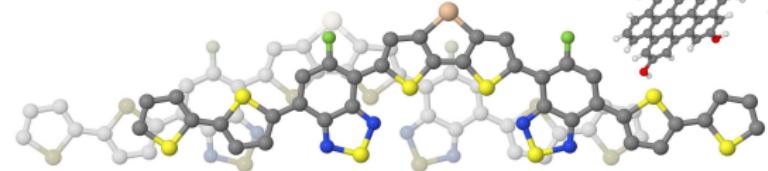
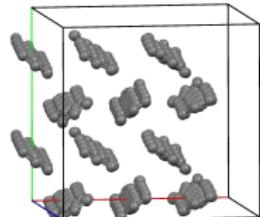
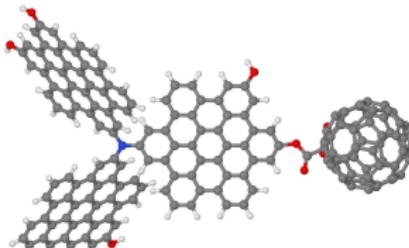
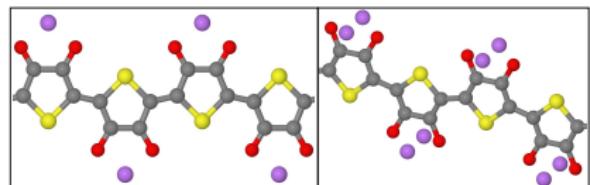
(Harrison's parameterization)

- Also **metal-organic** – include *d*-elements via  $pd\pi$
- Also **hybrid** – include any electronic system in resonance

*Number of organic semiconductors is comparable to number of inorganic ones*  
*Display is an example of a competitive application*

## Intro 2/4: Structural diversity

From 0D to 3D, from rigid to soft, often heterogeneous with multiscale structuring



# Intro 3/4: Some applications of organic semiconductors

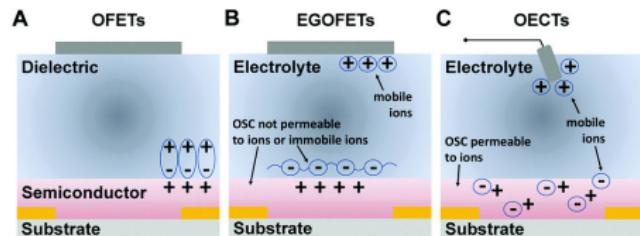
Any electronic device can be made all-organic

Light emitters (most successful)



Adv Mater 33, 2005630 (2021)

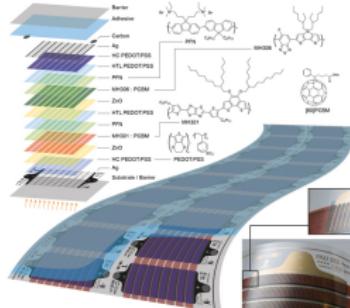
Transistors (most ubiquitous)



J Mater Chem C 6, 11778 (2018)

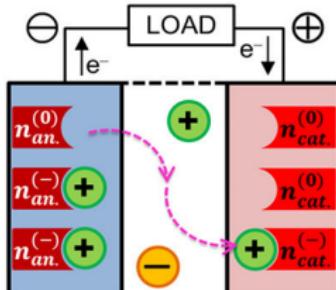
Solar cells (approaching 20% PCE)

Adv Energy Mater 11, 2002653 (2021)



Energy Environ Sci 7, 2925 (2014)

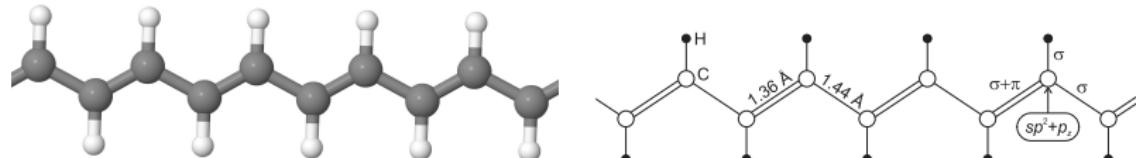
Batteries (early research)



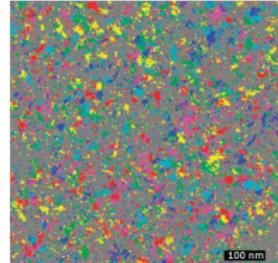
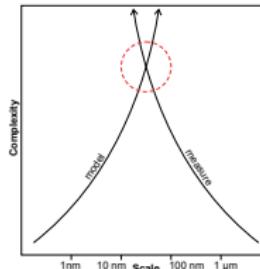
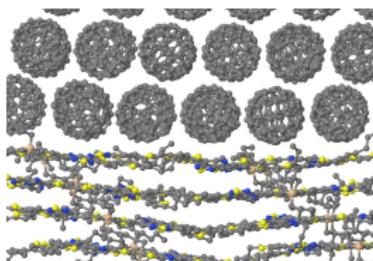
Chem Rev 120, 6490 (2020)

## Intro 4/4: Challenges in modeling organic semiconductors

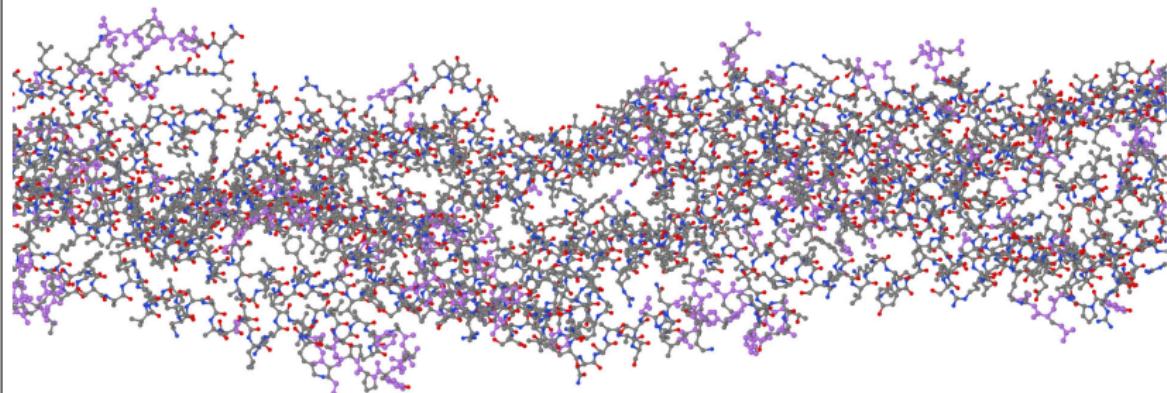
- Electron-electron correlations in low dimensional systems
  - ▶ Trans-polyacetylene (tPA) – 5 electrons in repeating unit – smallest real-world material for which majority of mainstream approaches fail



- Strong mode-specific electron-phonon coupling + soft structure
  - ▶ tPA – Peierls transition (C–C bond stretching mode) and solitons
  - ▶ Bond Length Alternation (BLA)
  - ▶ polaron formation
  - ▶ vibronic progression in spectra
- Scale gap problem – what is modeled is not what is measured



# Electronic Coarse-Graining (ECG)



10k non-H atoms  $\implies$  50k valence molecular orbitals (MOs) or 1M AOs

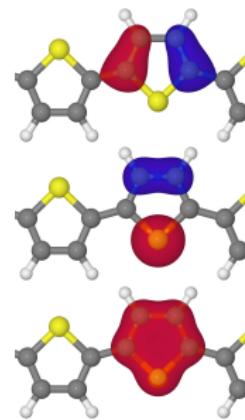
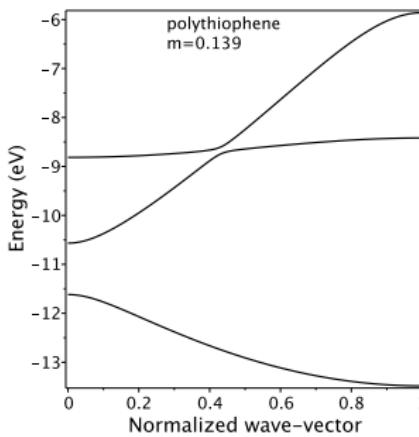
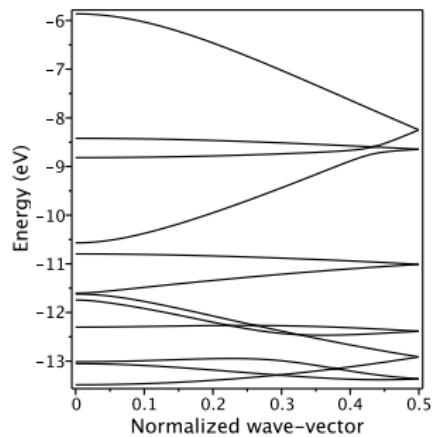
**ECG idea/goal:** Get minimal basis providing accurate description of a particular electronic property under molecular fluctuations  
(large-scale/low-energy electronic phenomena: UV-Vis spectra, transport)

## Requirements:

- Robustness of CG basis wrt molecular fluctuations
- Robustness and scalability of CG algorithm
- Quality control of CG basis and matrix elements

# ECG example 1/3: top of valence band of polythiophene

(full bands vs  $\pi$ -bands calculated from coarse-graining, basis reduction 83:3 for 6-31G\*)



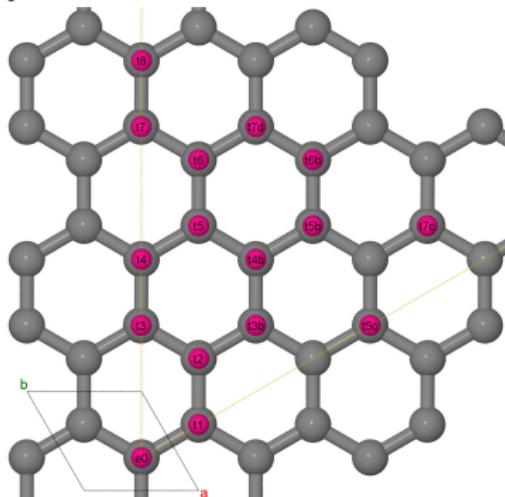
*At fixed geometry we can get numerically exact bands in a fixed energy range with substantial reduction in basis size*

## ECG example 2/3: band structure of graphene

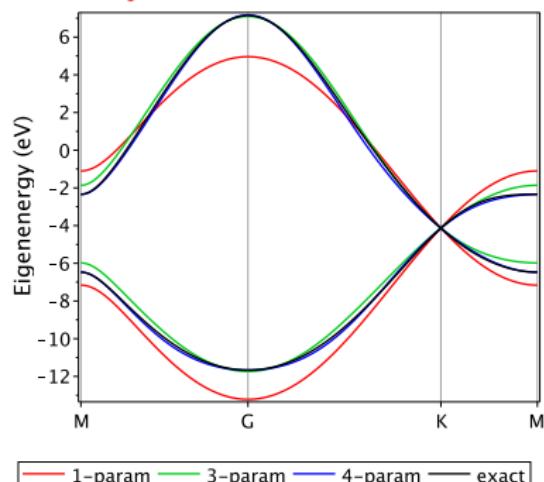
(mean field approximation for electrons, one can add explicit ee-interaction later)

$$\sum_{ij} H_{ij}^{1p} c_i^\dagger c_j \equiv \sum_i \varepsilon_i n_i + \sum_{i < j} t_{ij} T_{ij}, \quad n_i = c_i^\dagger c_i, \quad T_{ij} = c_i^\dagger c_j + c_j^\dagger c_i$$

here  $i, j$  enumerate CG sites,  $c_i$  describe quasiparticles (e, h, excitons),  
 $T_{ij}$  – kinetic energy term,  $\varepsilon_i$  – onsite energy,  $t_{ij}$  – transfer integral



Symmetry-unique transfer integrals

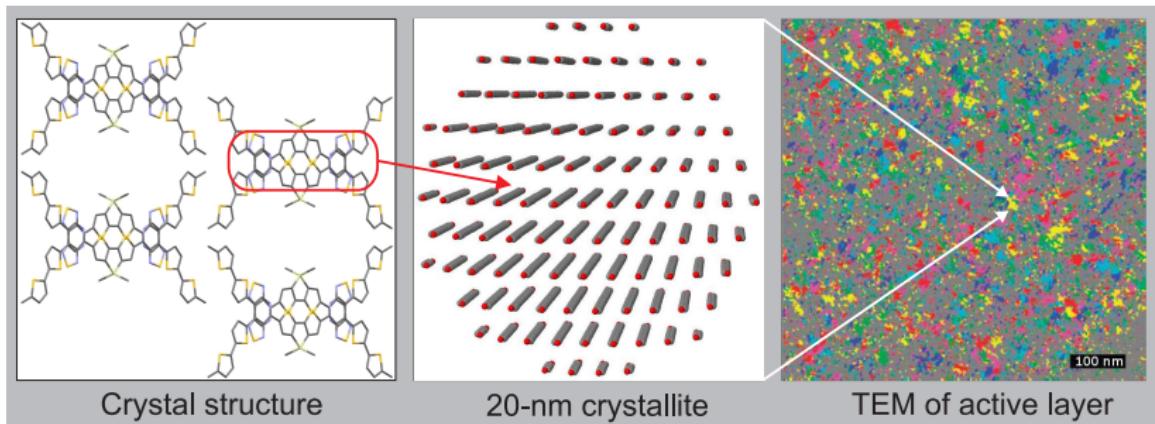


Energy bands of graphene  $\pi$ -system

*Simplifies first-principles parameterization of tight-binding models*

# ECG example 3/3: electronic transport in a molecular solid

(the simplest model, CG site = molecule *Annu Rev Phys Chem* 66, 305 (2015))



- Coarse grain electrons to **one site per molecule**
- Simplify molecular motions to harmonic vibrations
- Linearize coupling between electrons and molecular motions

$$\Rightarrow \sum_{ij} H_{ij}^{1p} c_i^\dagger c_j + \sum_\alpha \hbar \omega_\alpha \left( b_\alpha^\dagger b_\alpha + \frac{1}{2} \right) + \sum_{ij\alpha} \hbar \omega_\alpha g_{ij\alpha} (b_\alpha^\dagger + b_\alpha) c_i^\dagger c_j$$

Then solve this Hamiltonian (e.g. in small polaron hopping approximation)

*Provides one-electron basis for complex models*

# Methods of electronic coarse-graining (ECG)

## Algorithm

1. Determination of coarse-grained (CG) basis
2. Parameterization of tight-binding Hamiltonian
3. Quality control (for new systems)

ECG might often look trivial but here “the devil is in the details”, so there are many challenges:

- Large systems (large supercells)
- Entangled bands (overlapping in energy or hybridized)
- Cluster approximation to infinite systems
- Complex cases (e.g. excited states, no fixed SCF)
- Parameterization of complex models (e.g. electron-phonon)
- SCF and total energy in CG-basis

# Determination of coarse-grained (CG) basis

In what follows we consider coarse-graining of molecular orbitals (MOs)

## Algorithm

1. MOs of interest must be representable in CG basis  
     $\Rightarrow$  CG MOs are usually **localized MOs (LMOs)**
2. Tight binding parameters  $\varepsilon_i$  and  $t_{ij}$  are obtained by **projection of the Fock matrix of model fragments onto LMOs**
3. Effective Hamiltonian of a large system is obtained by its **fragmentation into the model fragments**

## Why LMO-based approach is working:

- Slater determinant is invariant under rotations of 1e orbitals
- Locality of phenomena: locality of 1e-density matrix and Hamiltonian, often only local SCF is important

[V Heine, Solid State Phys 35, 1 (1980)]

## Localization of molecular orbitals for coarse-graining

- Localization procedure is not unique Acc Chem Res 47, 2758 (2014) (trade off between spatial and energy localization)
- Projection approaches are **scalable and robust**
- Localization to unit cell is performed by Wannier functions
- The largest problem is bands entanglement (e.g.  $\pi$  and  $\sigma$ )
- LMOs can be used to get SCF (MOZYME code in MOPAC, fragmentation methods Chem Rev 112, 632 (2012))

### Algorithm

1. Reduce to unit cell (Wannier, or cluster in PBC or OBC)
2. Define projector (quality of the projector is critical)
3. Select initial MO subspace, project, and refine MOs
4. Convert LMOs to CG-basis (e.g. by block diagonalization)

# Projecting MO to LMO

Open-source code MolMod/LocalizeMO

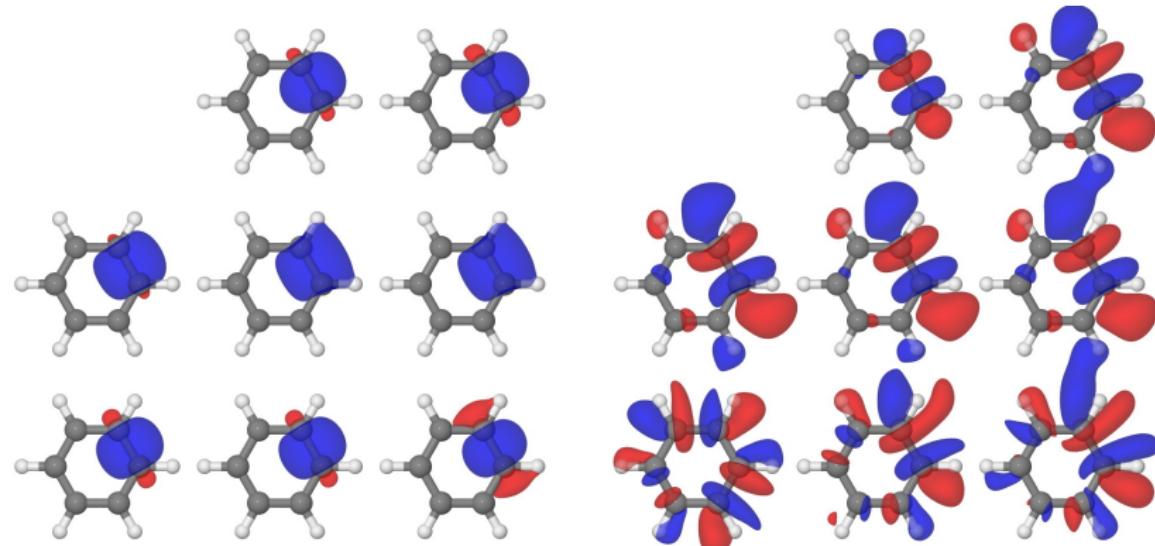
Project on/in/out by SVD of  $M^+SL$  or  $M^+P'SPM$ ,

where  $S$  – overlap,  $M$  – MOs,  $L$  – pre-LMOs,  $P$  – projector

Possible projector: subset of AOs (geometrical fragmentation)

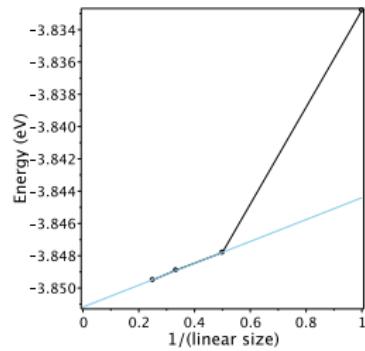
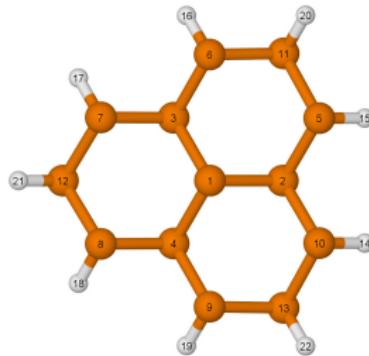
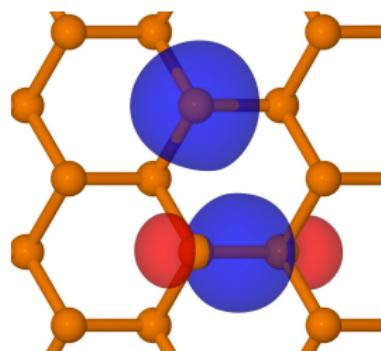
Possible pre-LMOs: LMOs by other method ('ad hoc' approach)

Example: benzene  $\sigma$  and  $\sigma^*$  LMOs (NBO/on/in/out/...)



# Locality and fast convergence of tight-binding parameters...

Illustrated by NBO analysis of the valence band of blue (A7) phosphorene

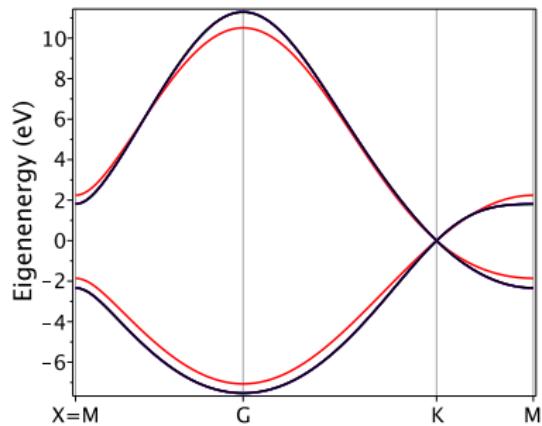


- There are two symmetry unique NBOs
- Error in estimation energy difference between them is 270 meV for the smallest cluster and 42 meV for the next one in series
- Error in estimation coupling between them is 18 meV for the smallest cluster and 3 meV for the next one in series

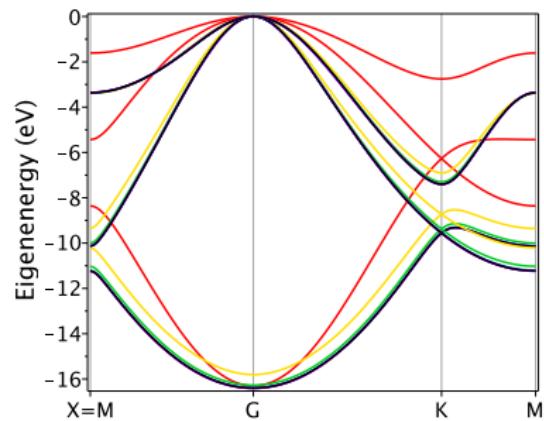
*Already the smallest fragment can be used for transfer integrals*

# ... small clusters are enough for parameterization

Example of hydrogen-passivated graphene clusters – graphene nanoflakes



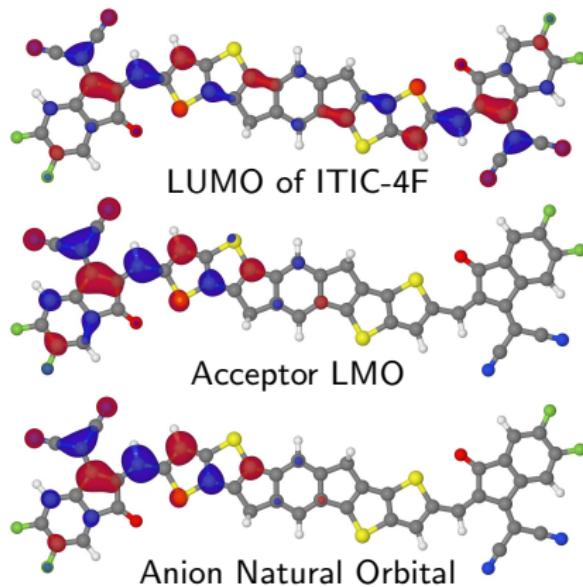
Graphene  $\pi$ -band  
(24-atom cluster is enough)



Graphene valence  $\sigma$ -band  
(54-atom cluster is enough)

# Quality control: Robustness of CG-basis wrt fluctuations

Example of A-D-A molecules as non-fullerene acceptors for solar cells



Compare various ECG models:

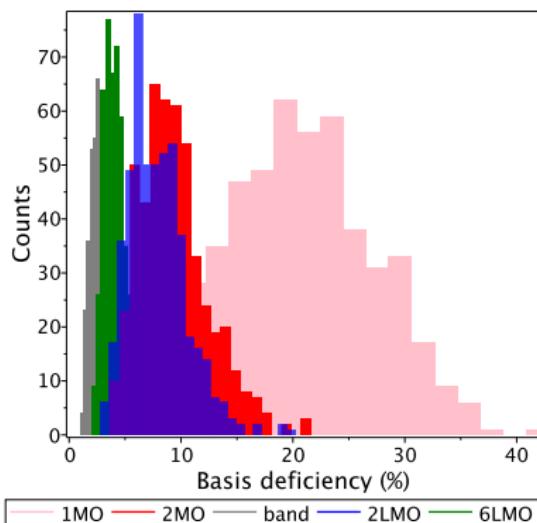
- simple-to-implement 1-site vs 2-site
- simple-to-implement 2-LUMO vs 2-LMO

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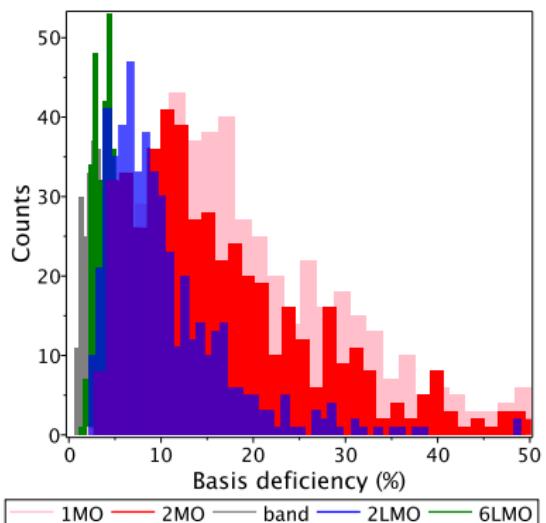
MO=Molecular Orbital, LUMO=Lowest Unoccupied MO, LMO=Localized MO

## 2-LMO model is the most appropriate

Statistical analysis of the basis deficiency in a coarse-grained description of electron MO and NO (i.e. LUMO and anion NO):



Electron NO in crystal  
(dynamic fluctuations)  
⇒ 1-site model fails



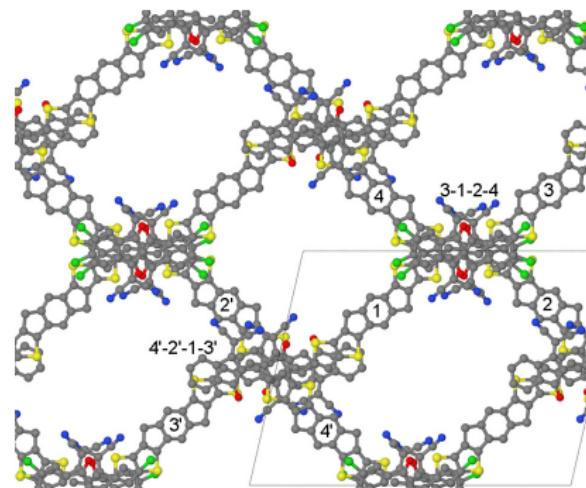
Electron MO in amorphous solid  
(dynamic+static fluctuations)  
⇒ 2-LUMO model fails

# Applications of electronic coarse-graining

- Electronic structure of an infinite system from calculations of its fragments (if conventional methods are unsuitable)
- Basis optimization and calculation of matrix elements of electron-phonon Hamiltonian (or other Hamiltonians)
- Basis optimization for non-adiabatic molecular dynamics
- In-depth analysis of electronic structure including map of electronic connectivity
- Generation of high-level descriptors for machine learning
- Hybrid approaches like QM/TB
- **Usually combination of the above items**

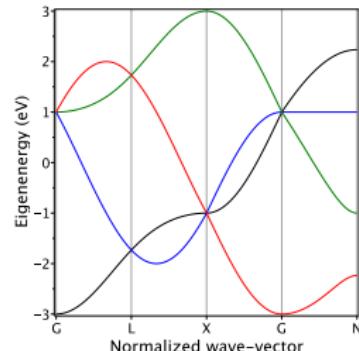
# Appl: Electronic structure of organic semiconductors

PBE-D3 is good for packing, but nonlocal functionals are needed for electronic properties

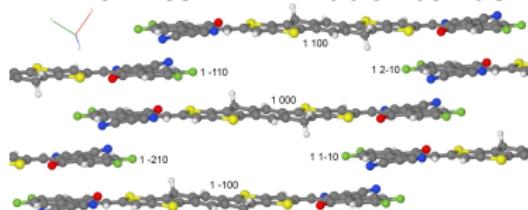


Wire-mesh packing  
(ITIC-2Cl/asym, o-IDTBR, Y6)

Chem Mater 33, 966 (2021)



Wire-mesh K4-model bands



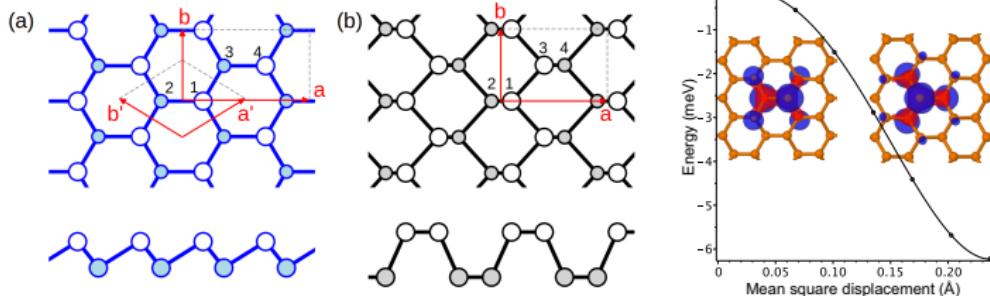
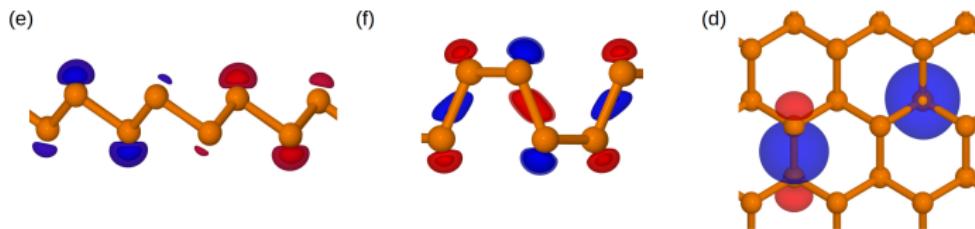
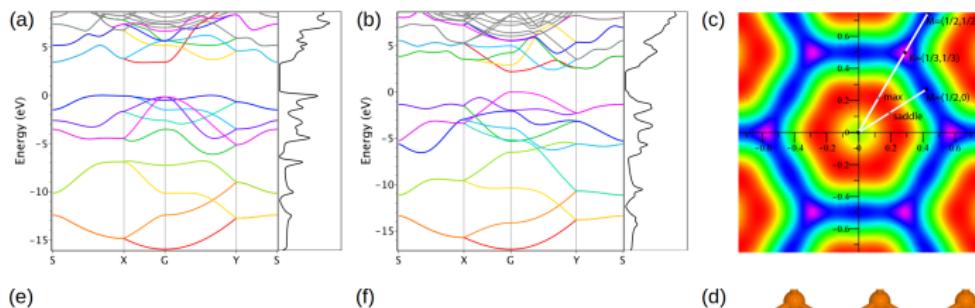
Brickwork packing (ITIC-4F)

**Solution:** Coarse-grain to a few sites per repeating unit, then parameterize TB Hamiltonian from cluster calculations

See computational protocol here: <https://zhugayevych.me/CMS/protocols.htm#molcry.ecg>

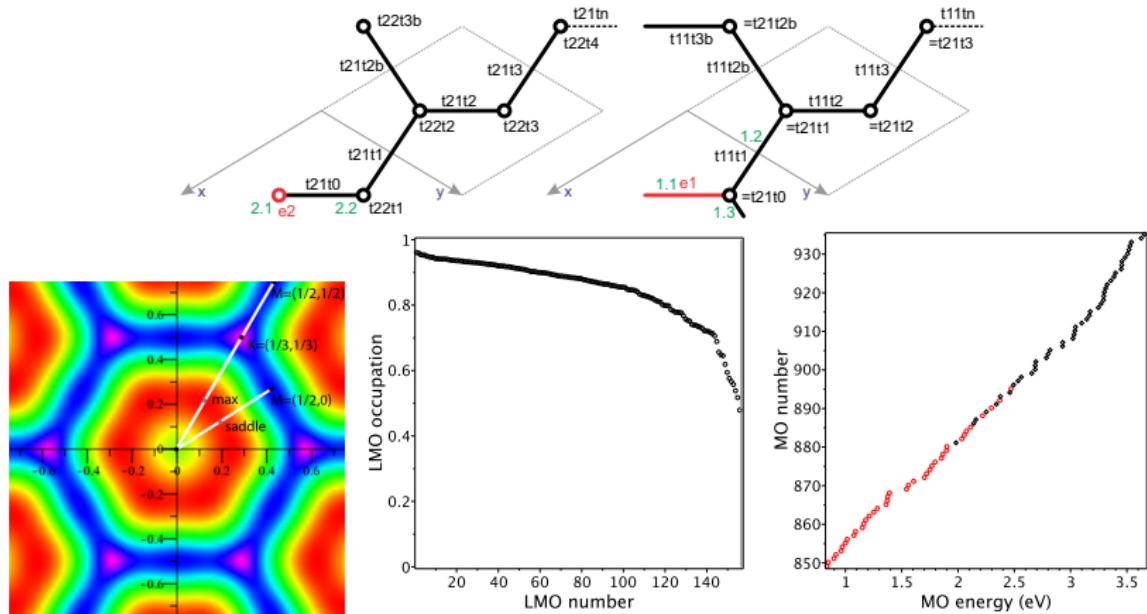
# Appl: Electronic structure of inorganic semiconductors...

Holes in blue-P form polarons, but not in black-P *J Phys Chem Lett* 12, 4674 (2021)

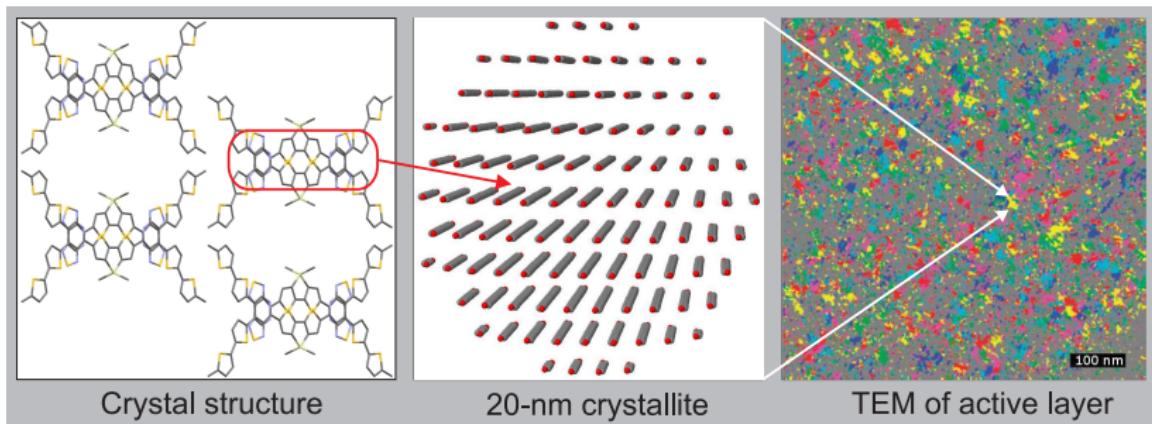


# ... tight-binding Hamiltonian of 2D pnictogens (with nonlocal density functionals, and also in polaron geometry)

- NBOs are used as projection basis for LMOs
- H-passivated clusters are used to derive TB Hamiltonian



## Appl: Electronic transport in a molecular solid...



- Coarse grain electrons to one site per “rigid block”
- Simplify molecular motions to harmonic vibrations
- Linearize coupling between electrons and molecular motions

$$\Rightarrow \sum_{ij} H_{ij}^{1p} c_i^\dagger c_j + \sum_\alpha \hbar \omega_\alpha \left( b_\alpha^\dagger b_\alpha + \frac{1}{2} \right) + \sum_{ij\alpha} \hbar \omega_\alpha g_{ij\alpha} (b_\alpha^\dagger + b_\alpha) c_i^\dagger c_j$$

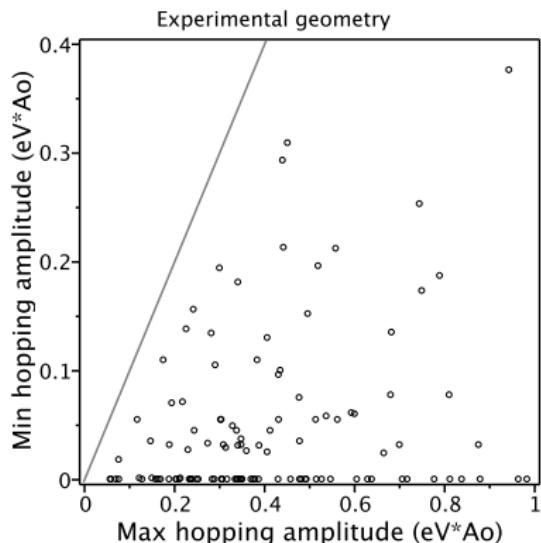
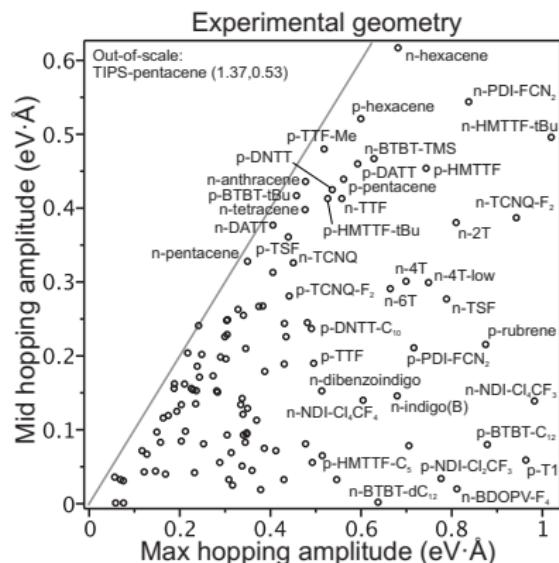
Then solve this Hamiltonian [Annu Rev Phys Chem 66, 305 \(2015\)](#)

*Provides one-electron basis for complex models. However, errors in calculation of charge carrier mobility might be large*  $\Rightarrow$

# ... calculate purely electronic descriptors

(electronic bandwidth, effective masses, hopping amplitudes)

Map of known crystalline organic semiconductors in terms of hopping amplitudes (~coupling multiplied by hopping distance):



$$\mu = 0.95 \frac{D(t^2)}{W(T)^2} \frac{\text{cm}^2}{\text{V}\cdot\text{s}}, \text{ square root of eigenvalues of } D(t^2) \text{ are hopping amplitudes}$$

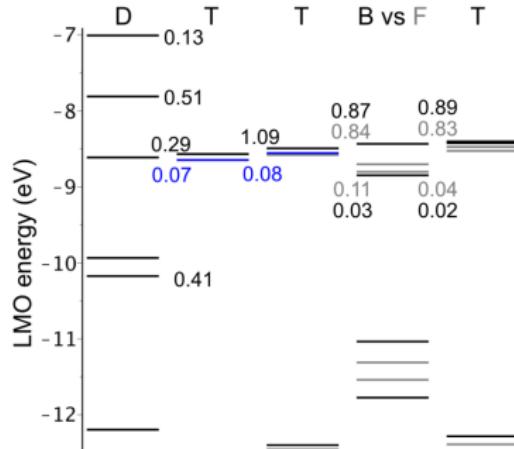
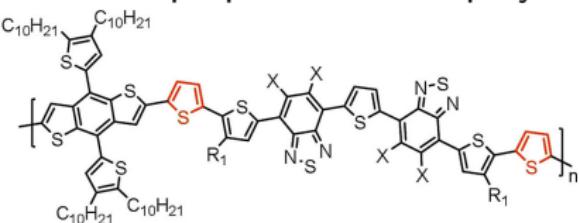
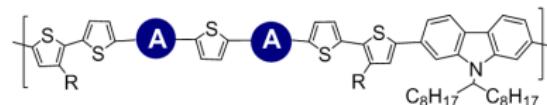
# Appl: Descriptors for LEGO-type design of polymers

(polymer properties from high-level descriptors calculated for small fragments)

Here TB Hamiltonian is used as descriptor OR for in-depth analysis

Synthetic Metals 259, 116231 (2020); Solar Energy 198, 605 (2020); Dyes and Pigments 185, 108899 (2021)

By changing monomers we tune functional properties of the polymer:



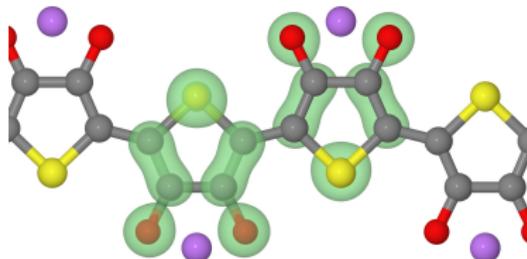
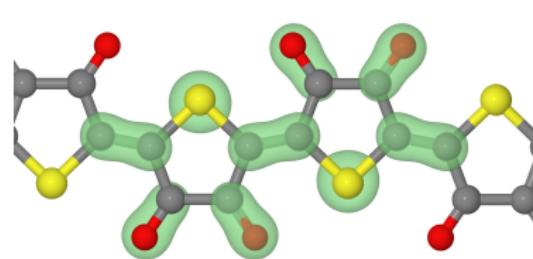
Analysis of the coarse-grained electronic Hamiltonian shows what happens with electronic structure ( $X=H$  vs  $F$ ):

# Appl: Analysis of rechargeable organic metal-ion batteries

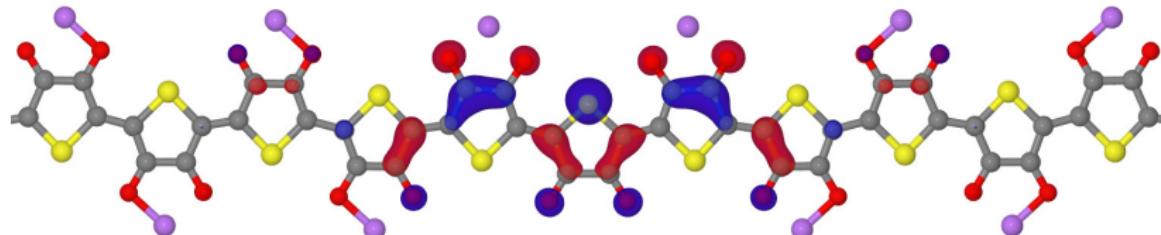
Problems (all-organic): poor electronic conduction, irreversible changes, no structural data

What happens if we dope/charge  $\pi$ -conjugated backbone:

A toy model of a flexible polymer with local doping/charging



Upon Li-intercalation  $p\pi$ -bonding pattern changes dramatically



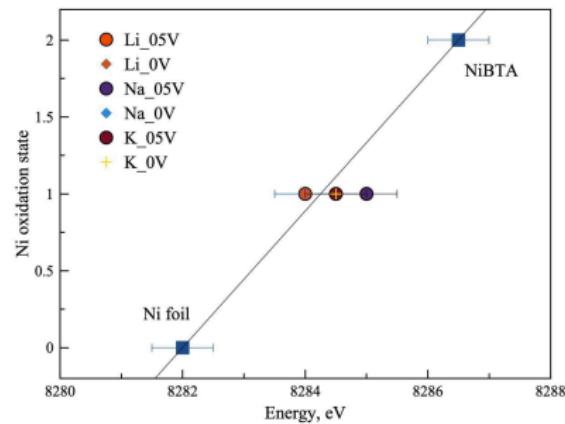
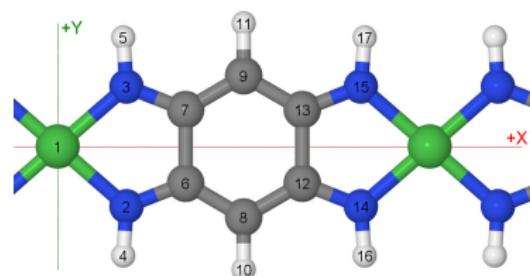
Deep electronic traps appear on Li-deficient monomers (-0.5 eV)

*Upon ion intercalation irreversible structural changes are expected*

# Appl: Metal-organic electrodes for batteries...

Ni-BTA polymer: reversible changes, structural data (operando XRD and Raman)

Chem Sci 13, 8161 (2022)

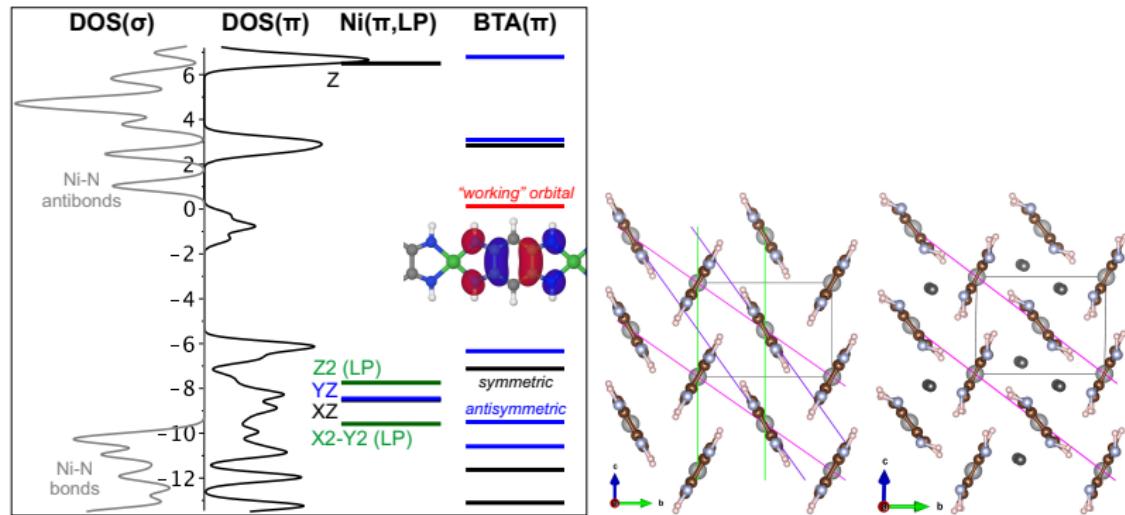


Questions to theoreticians (controversial published reports):

- Intermolecular packing (herringbone or  $\pi$ -stack, ions location)
- Electronic structure (metal or insulator, frontier orbitals)
- Interpretation of UV-Vis, Raman, and XANES spectra
- Mechanism of operation and role of transition metal...

# ... in-depth analysis of electronic structure

(localized molecular orbital analysis of  $\pi$ -system using proper density functional)



*Ni itself is electrochemically inactive but pre-charges\* (dopes) organic part of the  $\pi$ -conjugated polymer (BTA ligand)*

\* in analogy to  $\pi$ -backbonding Ni donates 2e through Ni-N  $\sigma$ -bonds but withdraws them back from BTA  $\pi$ -system, so that formally Ni is in  $\text{Ni}^{(0)}$  state

## Summary and Outlook

- Electronic coarse-graining is a powerful tool for modeling of electronic properties of organic semiconductors whenever the basis set size becomes computationally prohibitive for direct application of first-principle DFT calculations
- One of the main questions is whether ECG can be used as efficiently as molecular coarse-graining in classical force-fields

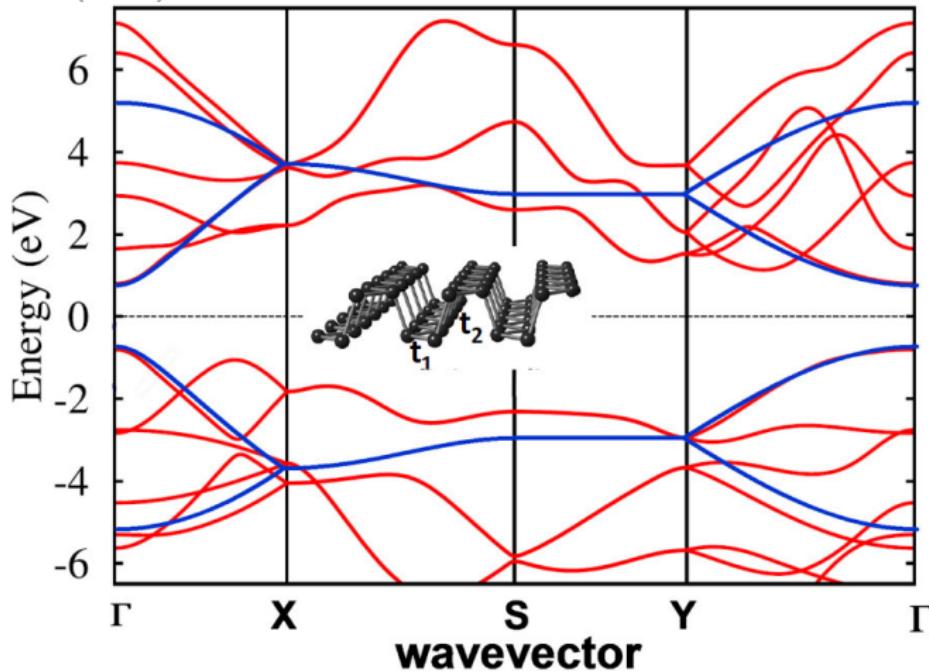
### Open problems

- Coarse-graining of excited states
- Efficient parameterization of electron-phonon models
- Generation of high-level descriptors for machine learning
- Basis optimization for non-adiabatic molecular dynamics
- Hybrid approaches like QM/TB
- SCF and total energy in CG-basis

# Appendix

# Fitting tight binding Hamiltonian

PRB 95, 075436 (2017)



*Great for simple systems and finite precision,  
ML is needed for non-simple systems and systematic refinement*

# Charge carrier mobility

Basic equations in homogeneous medium

$$\text{Current density} \quad j = \mu \cdot n \cdot e \mathcal{E}$$

Free charge carriers	Localized charge carriers
Drude formula	Hopping
$\mu = \frac{e \tau_{\text{scattering}}}{m_{\text{effective}}}$	$\mu = \frac{2\pi e}{\hbar} f \cdot (aV)^2 \frac{J}{T}$

\* Purely electronic and electron-phonon interaction terms are factorized

Scattering (or localization) mechanisms:

- dynamic lattice defects (phonons, intramolecular vibrations)
- extrinsic disorder: from lattice defects to mesoscopic nonhomogeneity (grain boundaries, interfaces, composites)
- carrier-carrier interaction

$f$  = lattice form-factor,  $a$  = lattice spacing,  $V$  = electronic inter-site coupling,  $J$  = spectral overlap, mobility definition  $v = \mu \mathcal{E}$ , zero-field mobility =  $eD/T$ , exciton diffusion length =  $\sqrt{D \cdot \text{lifetime}}$