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Electronic coarse-graining of long conjugated molecules: case study of non-fullerene acceptors

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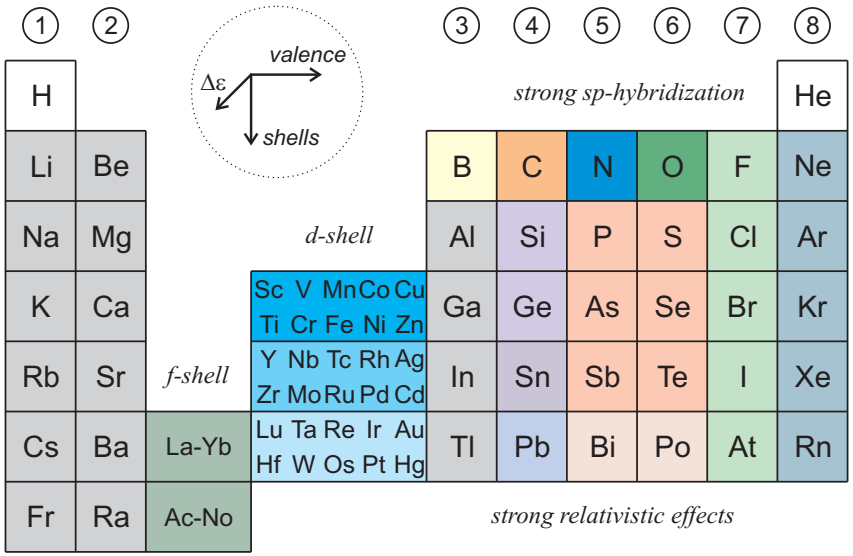
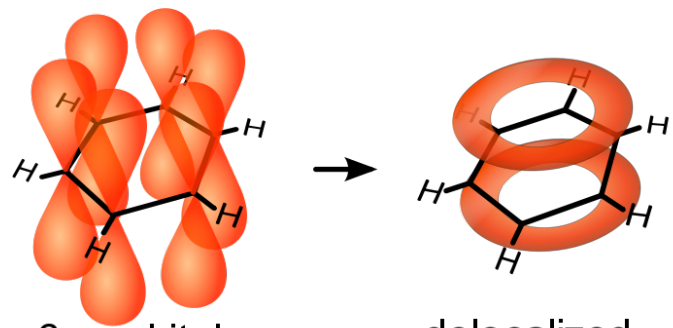
Intro 1/5: What is organic semiconductor

1. **Organic** – built from C with terminal H, possibly with isovalent substitutions (N for CH, O/S for CH_2, F/Cl for H)
2. π-**conjugated** – only π-electrons on frontier orbitals





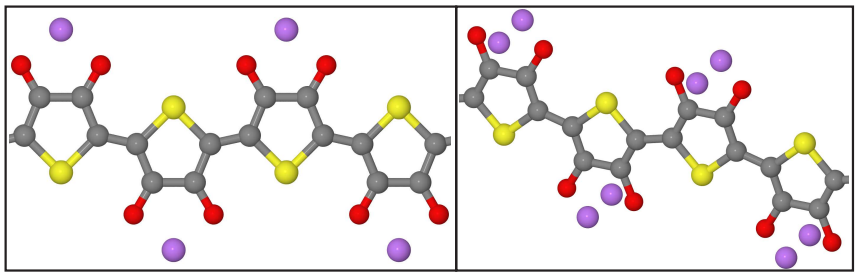
$$t_{sp2} = 3.26\frac{\hbar^2}{md^2} \gg t_{pp\pi} = 0.63\frac{\hbar^2}{md^2}$$
(Harrison's parameterization)

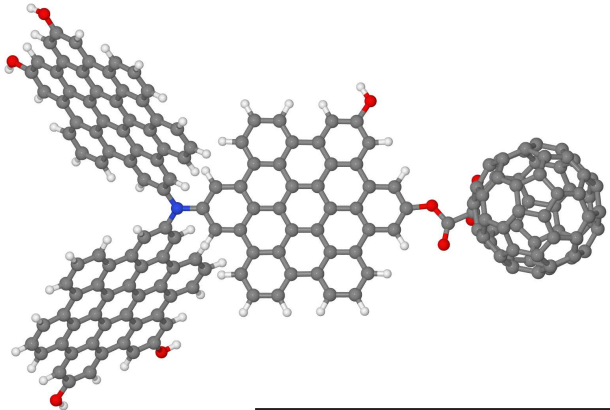
- Also **metal-organic** – include *d*-elements via $pd\pi$
- Also **hybrid** – include any electronic system in resonance

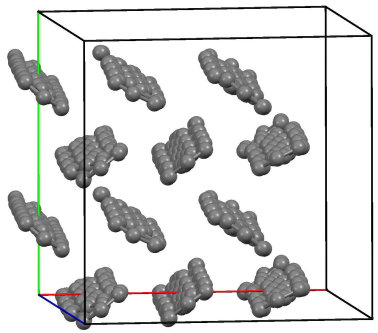
Number of organic semiconductors is comparable to number of inorganic ones
Display is an example of a competitive application

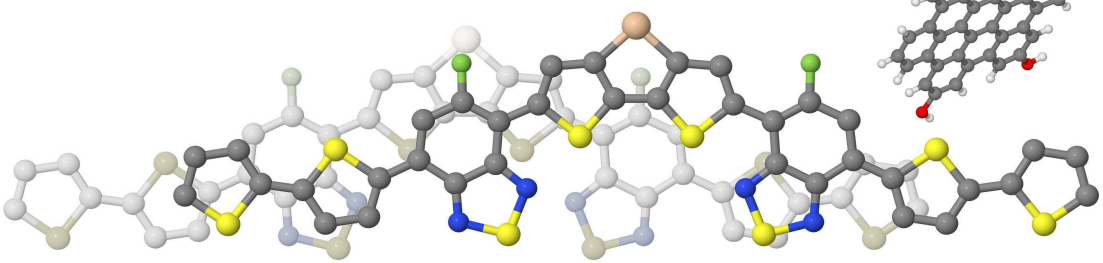
Intro 2/5: Structural diversity

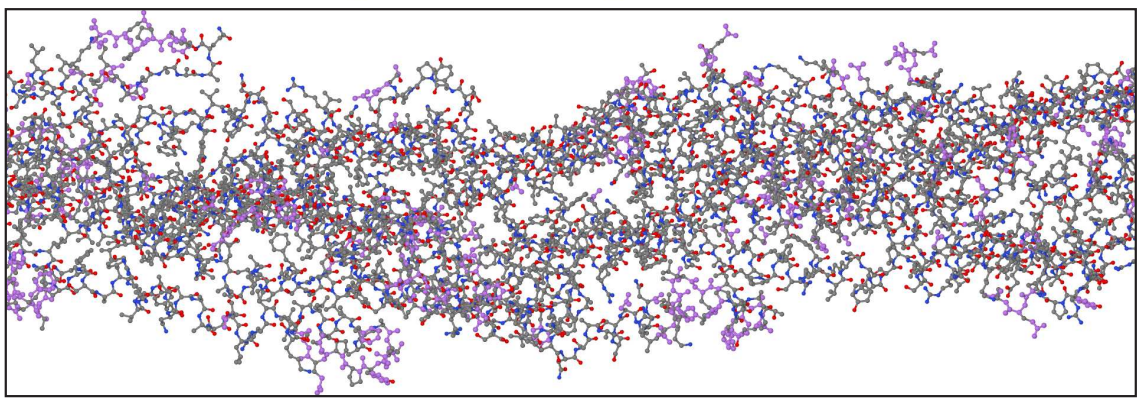
From 0D to 3D, from rigid to soft, often heterogeneous with multiscale structuring

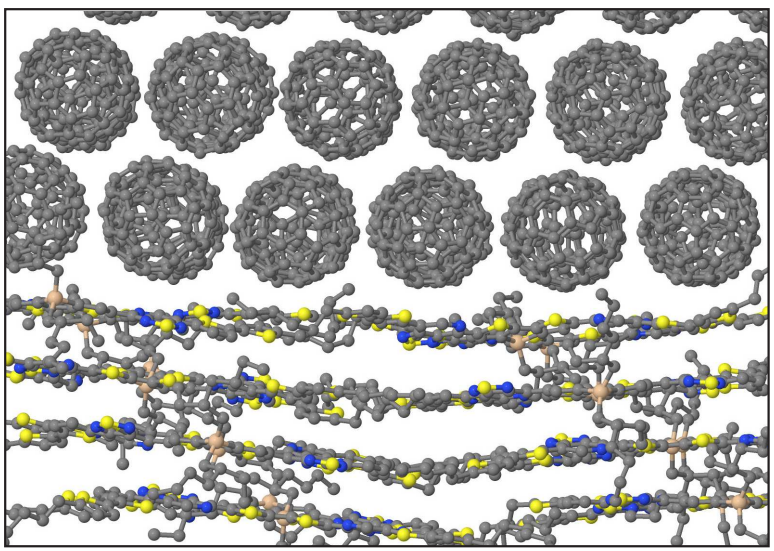












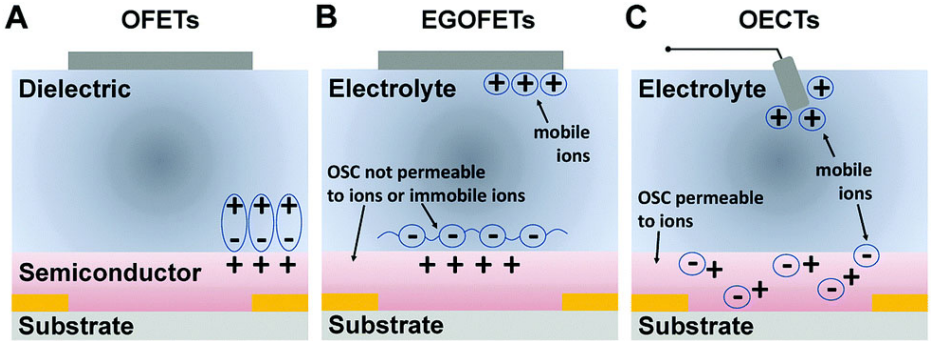
Intro 3/5: Some applications of organic semiconductors

Any electronic device can be made all-organic

Light emitters (most successful)

Adv Mater 33, 2005630 (2021)

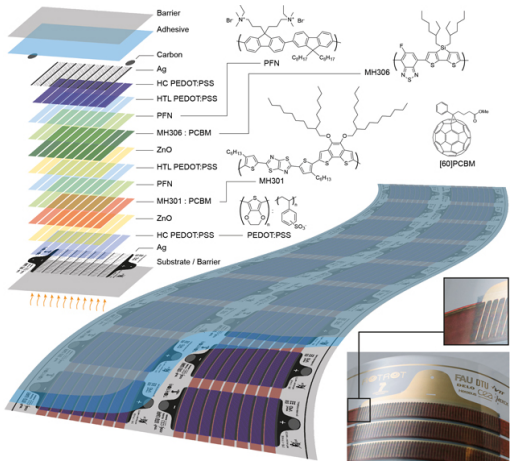
Transistors (most ubiquitous)



J Mater Chem C 6, 11778 (2018)

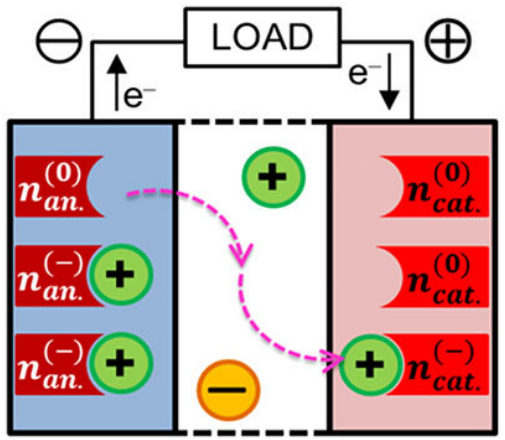
Solar cells (approaching 20% PCE)

Adv Energy Mater 11, 2002653 (2021)



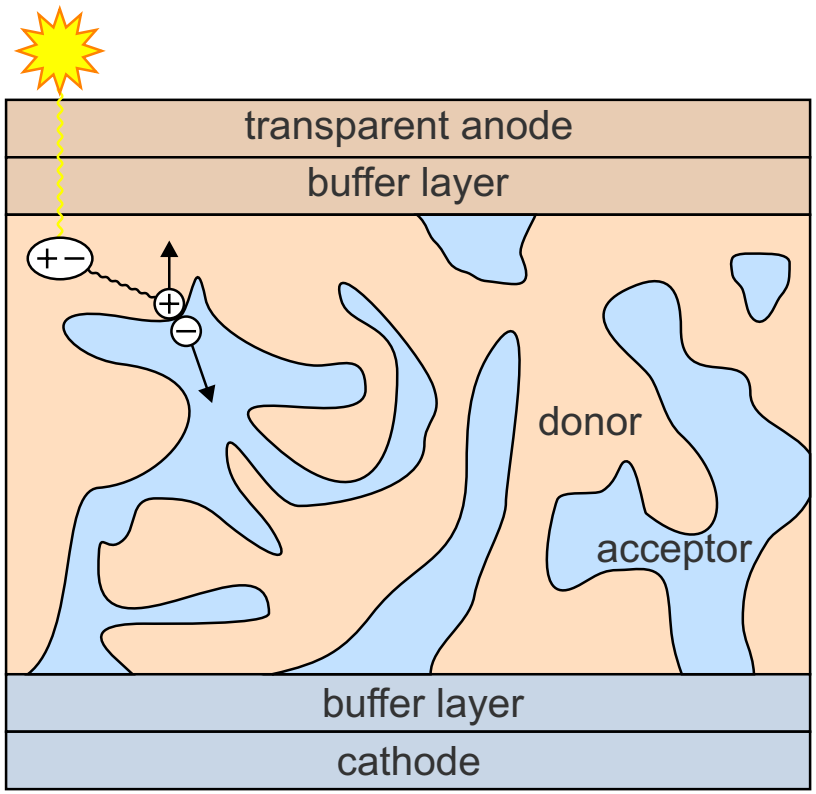
Energy Environ Sci 7, 2925 (2014)

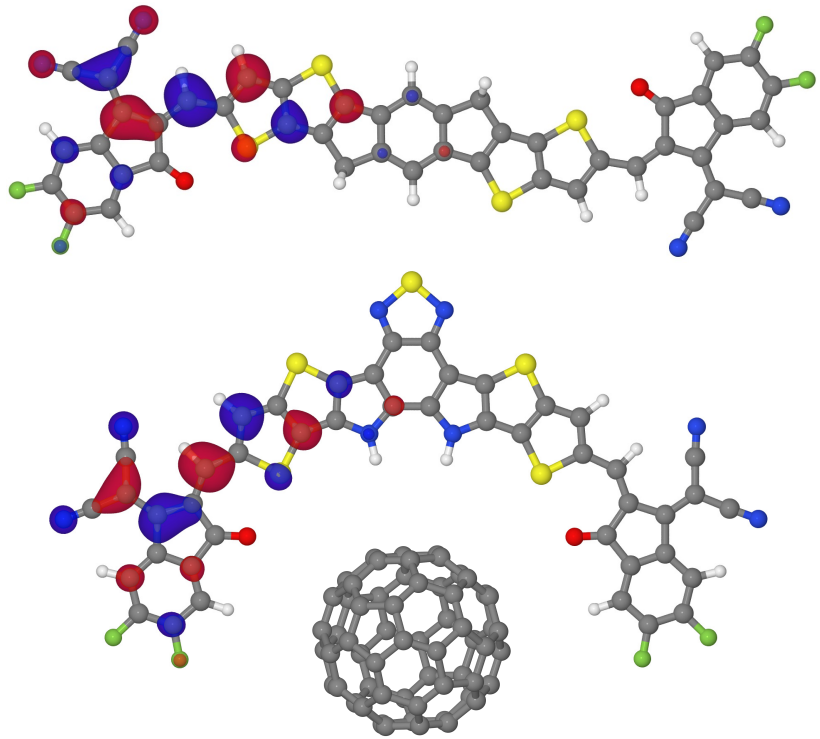
Batteries (early research)



Chem Rev 120, 6490 (2020)

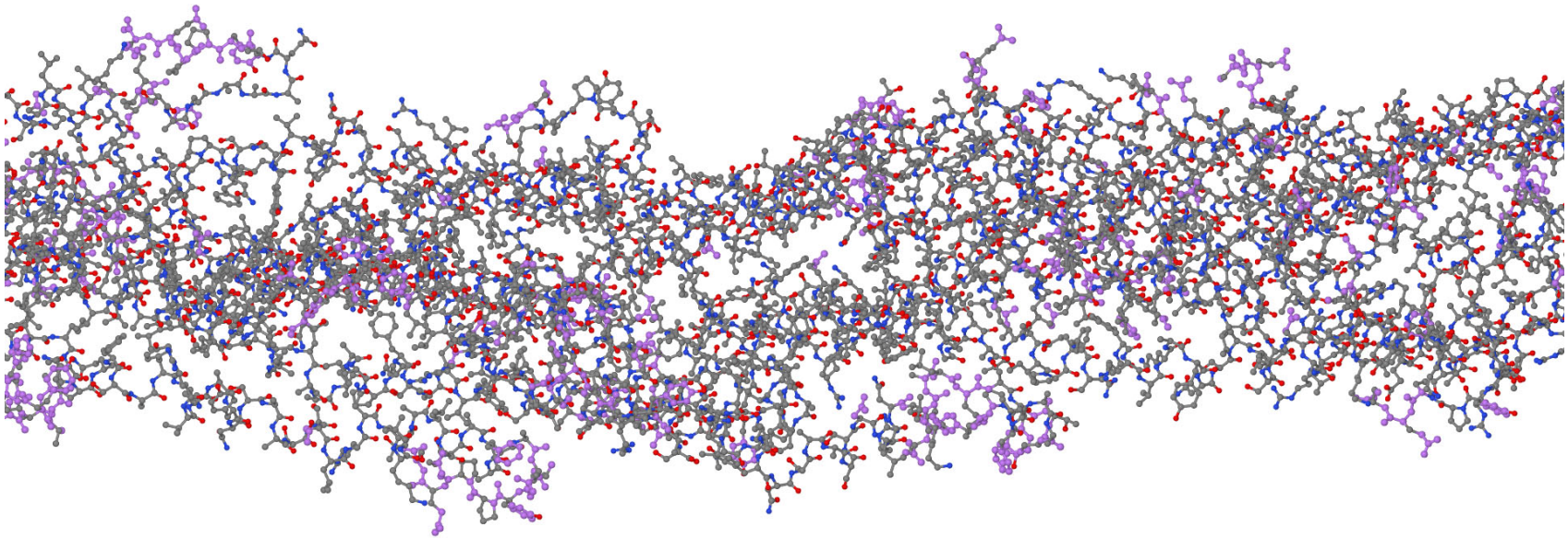
Intro 4/5: Non-fullerene acceptors (NFA) for solar cells





- Best performers have A-D-A structure
- Intramolecular A-A couplings (100-200 meV) are close to intermolecular (50-100 meV)
- Some NFA show 3D electronic connectivity Chem Mater 33, 966 (2021)

Intro 5/5: Electronic Coarse-Graining (ECG)



10k non-H atoms $\Longrightarrow$ 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

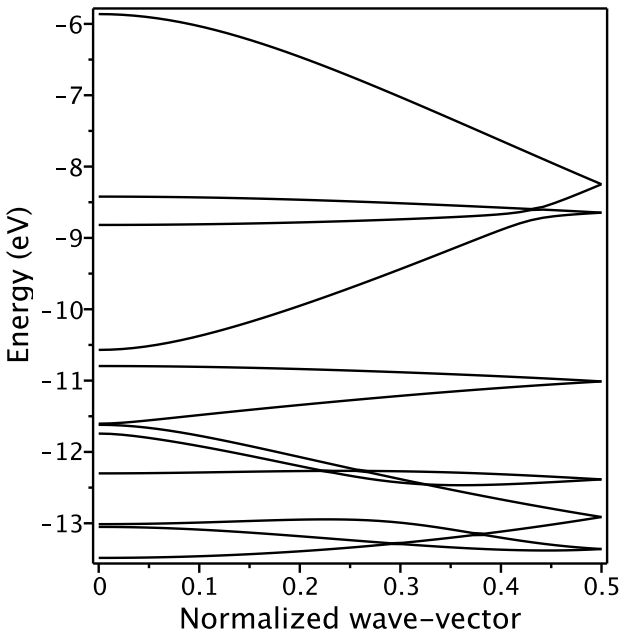
(large-scale/low-energy electronic phenomena: UV-Vis spectra, transport)

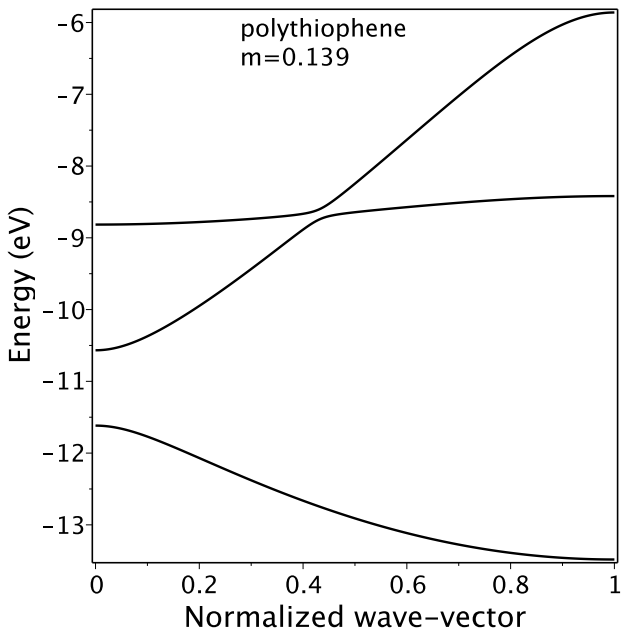
Requirements:

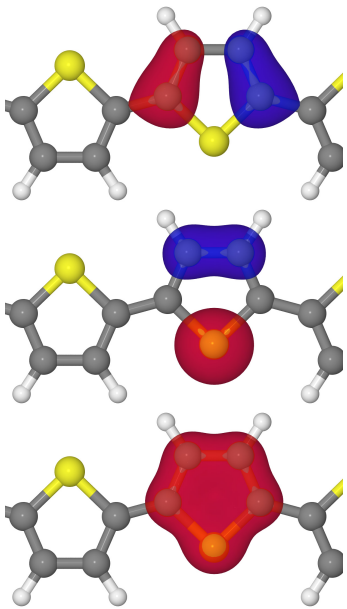
- Robustness of CG basis wrt molecular fluctuations
- Robustness and scalability of CG algorithm
- Quality control of CG basis and matrix elements

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

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





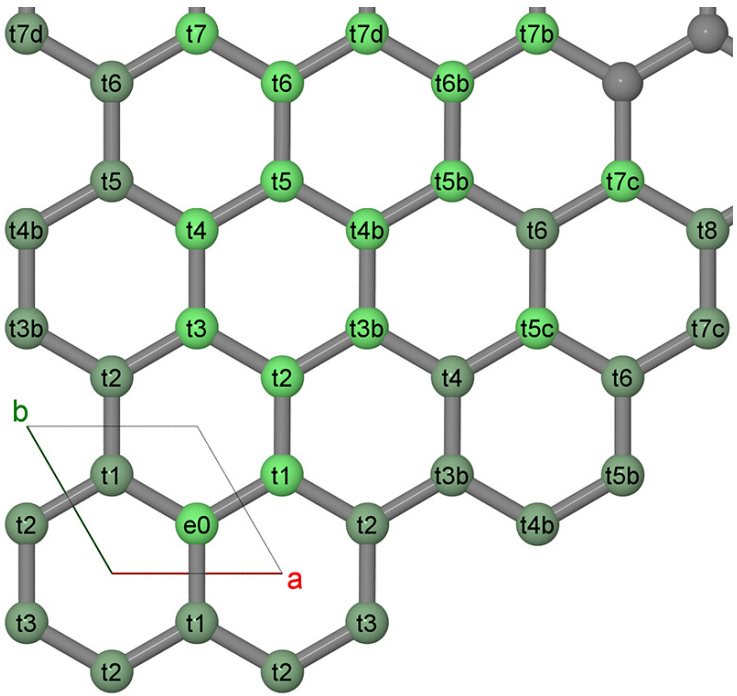


ECG example 2/3: band structure of graphene

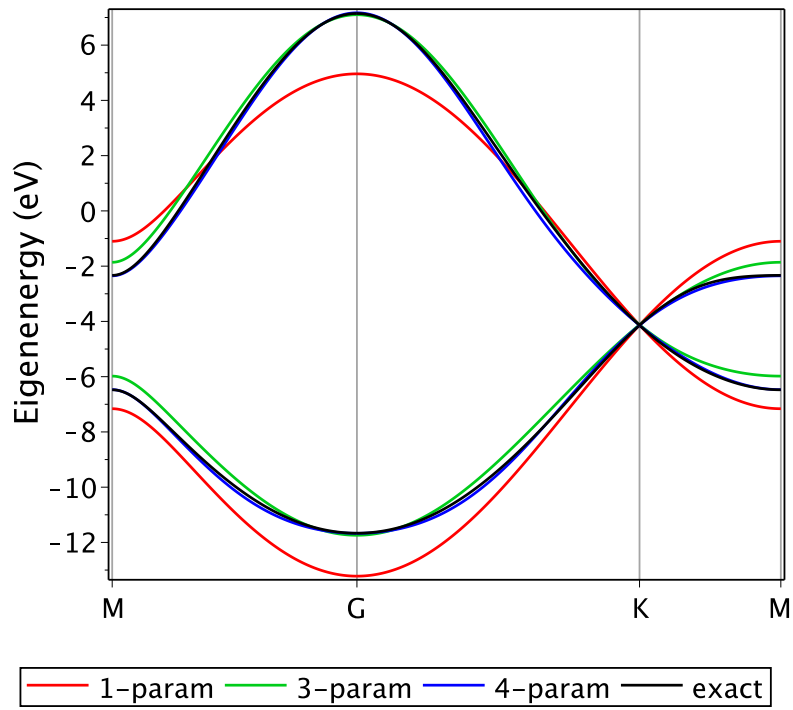
(mean field approximation for electrons, one can add explicit ee-interaction later)

$$\sum_{ij} H^{1p}_{ij} c^\dagger_i c_j \equiv \sum_i \varepsilon_i n_i + \sum_{i<j} t_{ij} T_{ij}$$

here i, j enumerate coarse-grained sites, c_i describe quasiparticles (electrons, holes, excitons etc.), ε_i – onsite energy, $n_i = c^\dagger_i c_i$, t_{ij} – transfer integral, $T_{ij} = c^\dagger_i c_j + c^\dagger_j c_i$ – kinetic energy

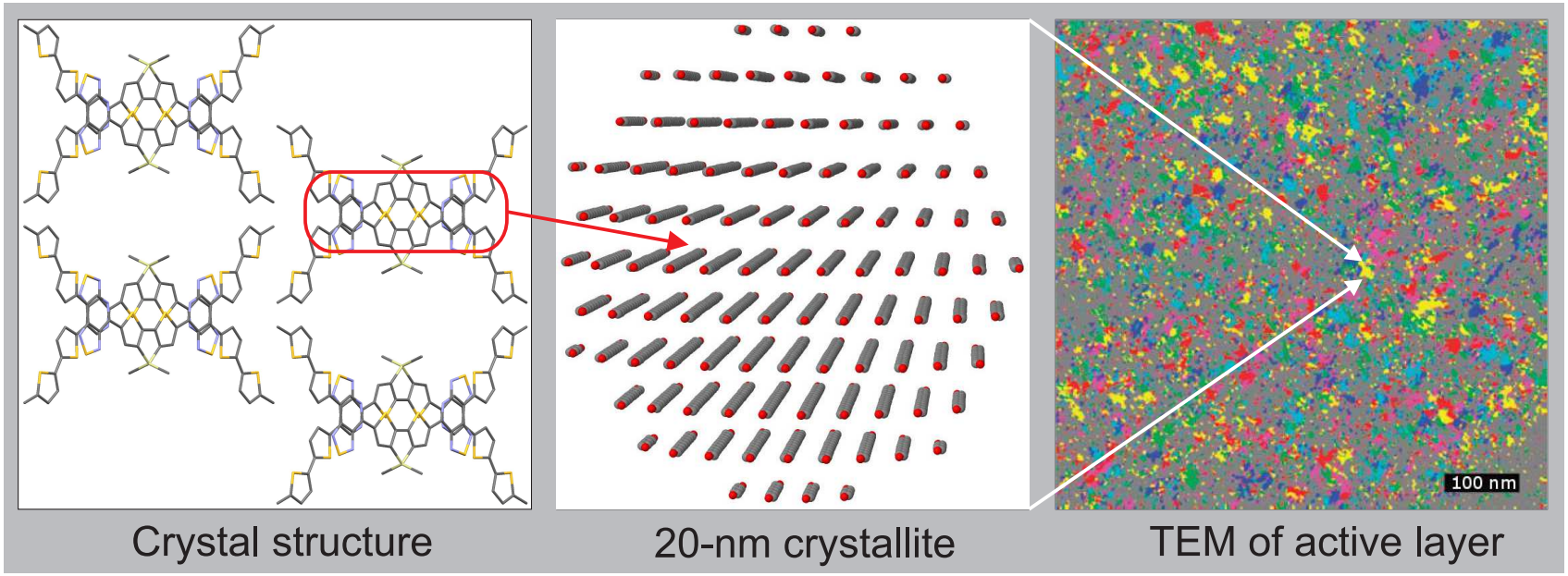


Symmetry-unique transfer integrals



Energy bands of graphene π-system

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



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

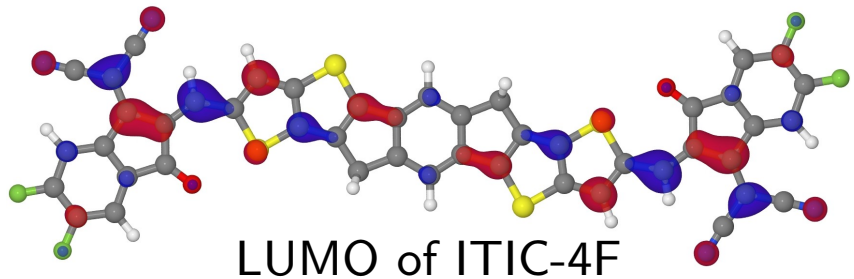
$$\Longrightarrow \sum_{ij} H_{ij}^{1p} c_i^\dagger c_j + \sum_{\alpha} \hbar\omega_\alpha \left(b_\alpha^\dagger b_\alpha + \frac{1}{2} \right) + \sum_{ij\alpha} \hbar\omega_\alpha g_{ij\alpha} \left(b_\alpha^\dagger + b_\alpha \right) c_i^\dagger c_j$$

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

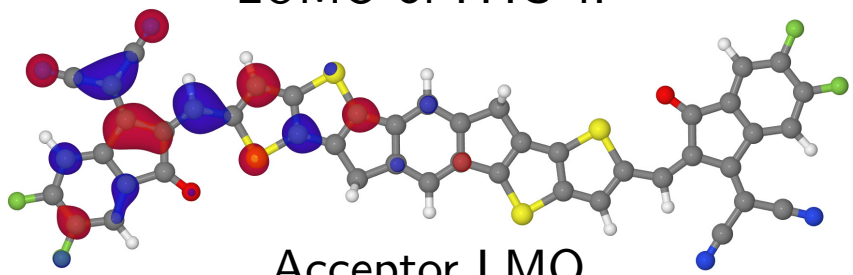
Annu Rev Phys Chem 66, 305 (2015)

Motivation: Córrect ECG of A-D-A molecules

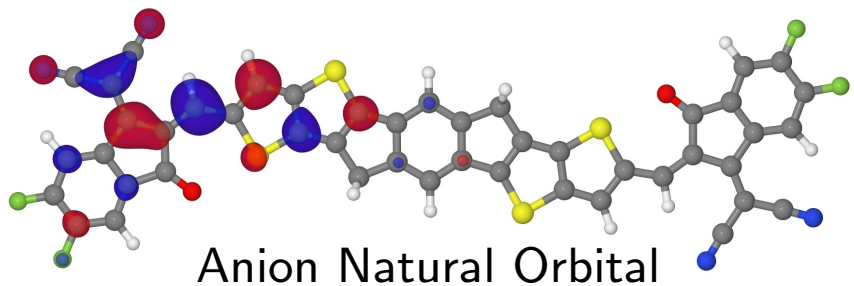
(for transport of electrons in a solid state at ambient conditions)



LUMO of ITIC-4F



Acceptor LMO



Anion Natural Orbital

Determine qualitative and quantitative errors of inaccurate ECG:

- Is electron localized on acceptor or delocalized over molecule?
- How inaccurate ECG influences charge transport parameters?
- To be compared: 1-site vs 2-site, 2-LUMO vs 2-LMO models

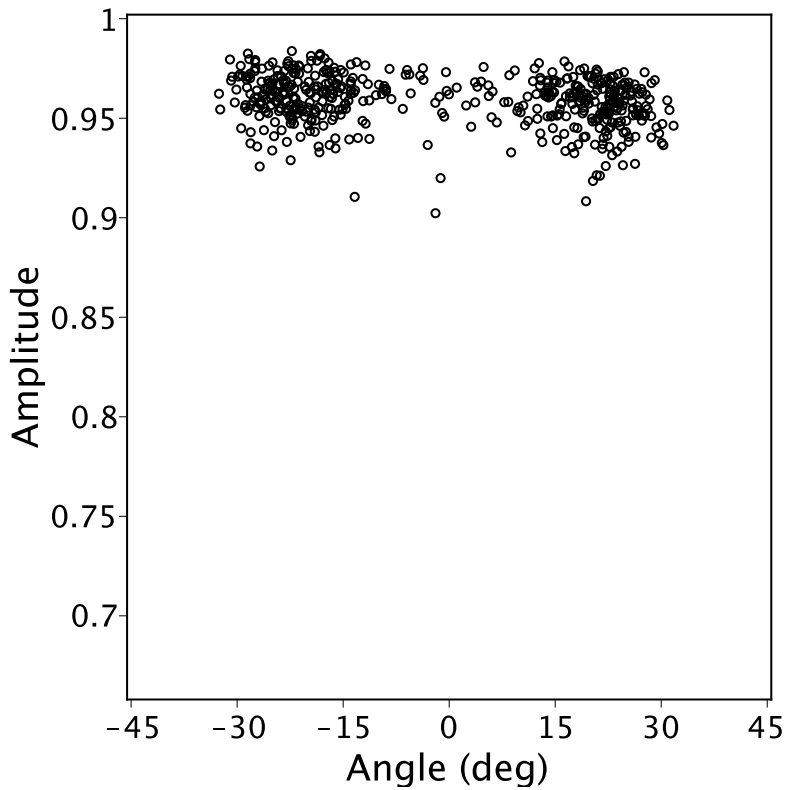
MO=Molecular Orbital, LUMO=Lowest Unoccupied MO, LMO=Localized MO

Methodology

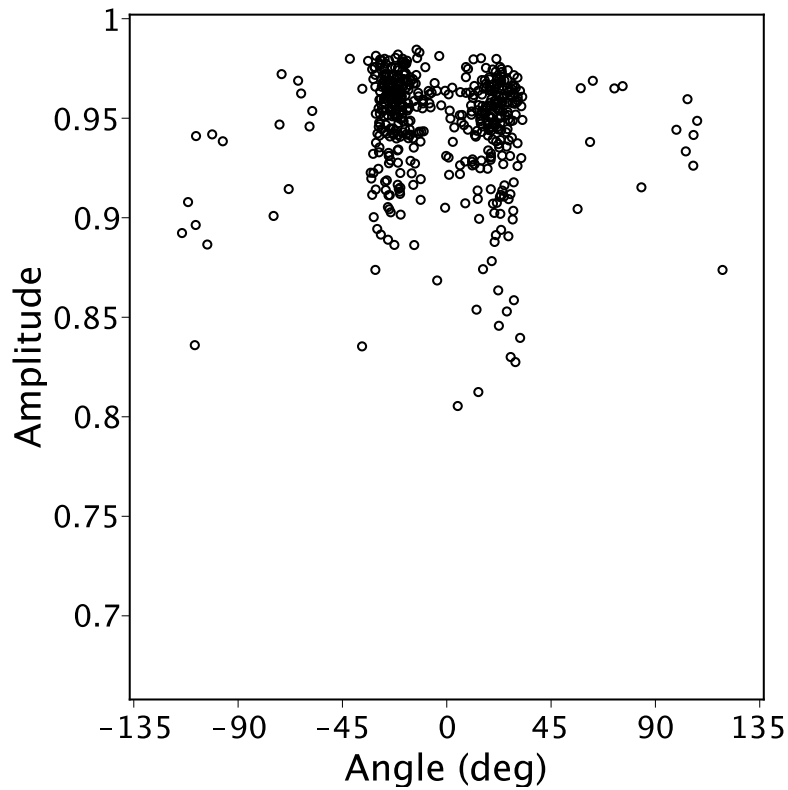
- Use Molecular Dynamics (MD) of ITIC-4F molecular solid to study influence of static and dynamic disorder on electronic structure of individual molecules
- Sample thermal vibrations of a single molecule to study influence of zero energy vibrations

Result 1/3: Electron is localized on acceptor

Coefficients of expansion of electron NO of distorted molecules in two LMOs in polar representation rotated by 45°:



Classical MD in crystal

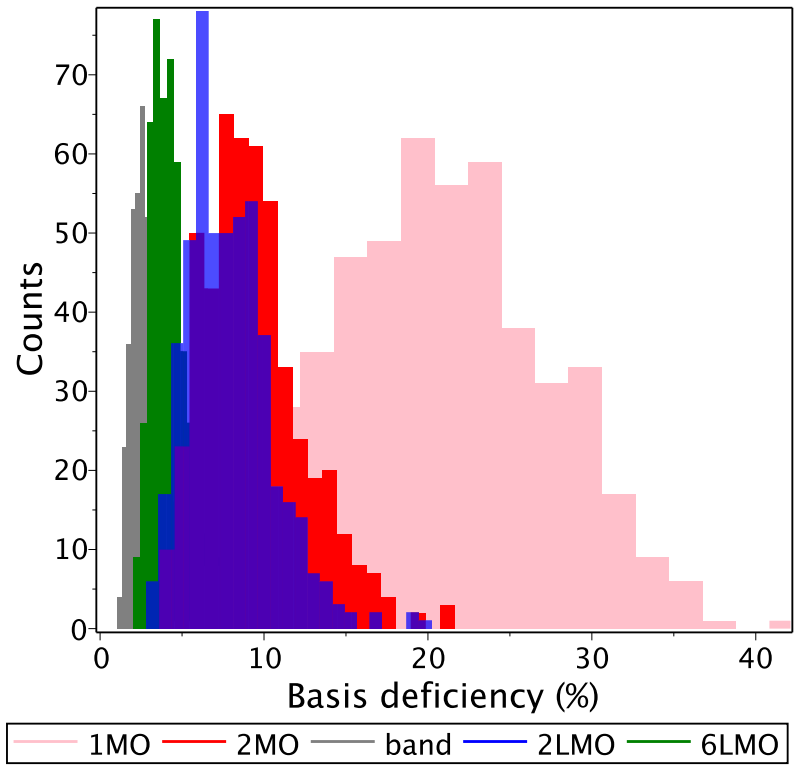


Classical MD in amorphous solid

NO=Natural Orbital, LMO=Localized Molecular Orbital, MD=Molecular Dynamics

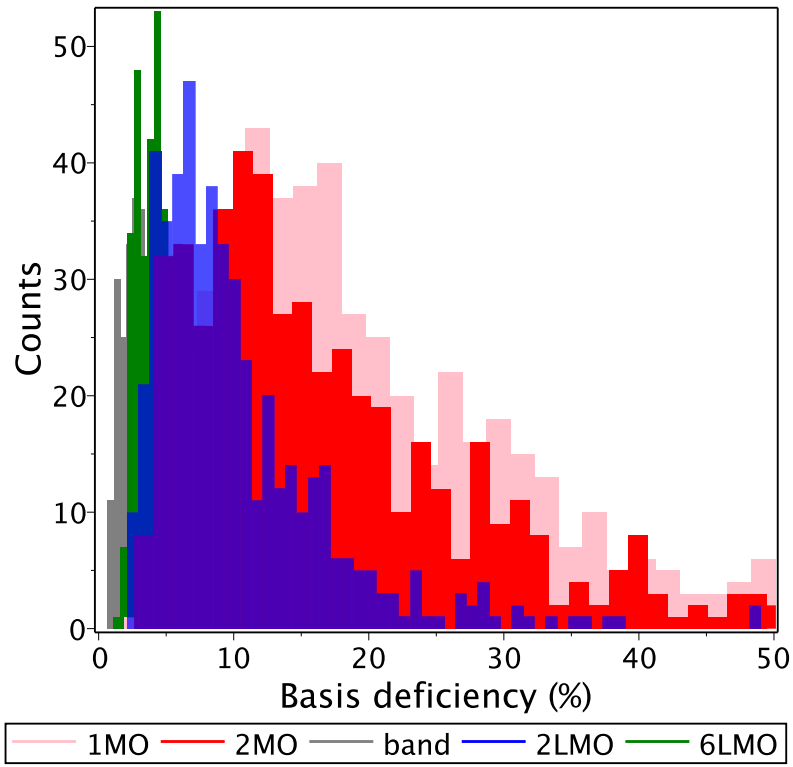
Result 2/3: 2-LMO model is the most appropriate

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

$\Longrightarrow$ 1-site model fails

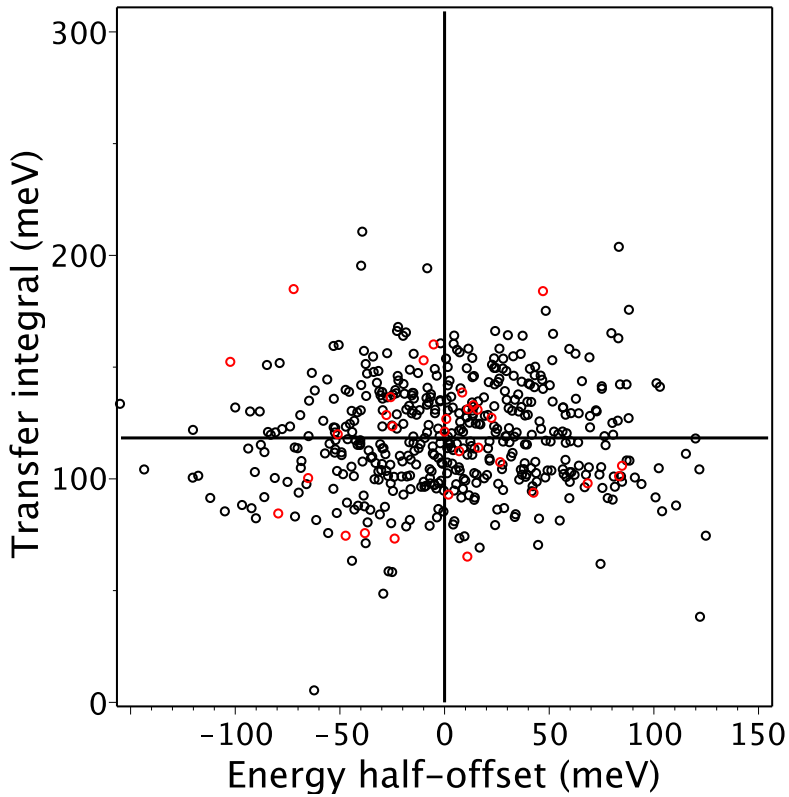


Electron MO in amorphous solid

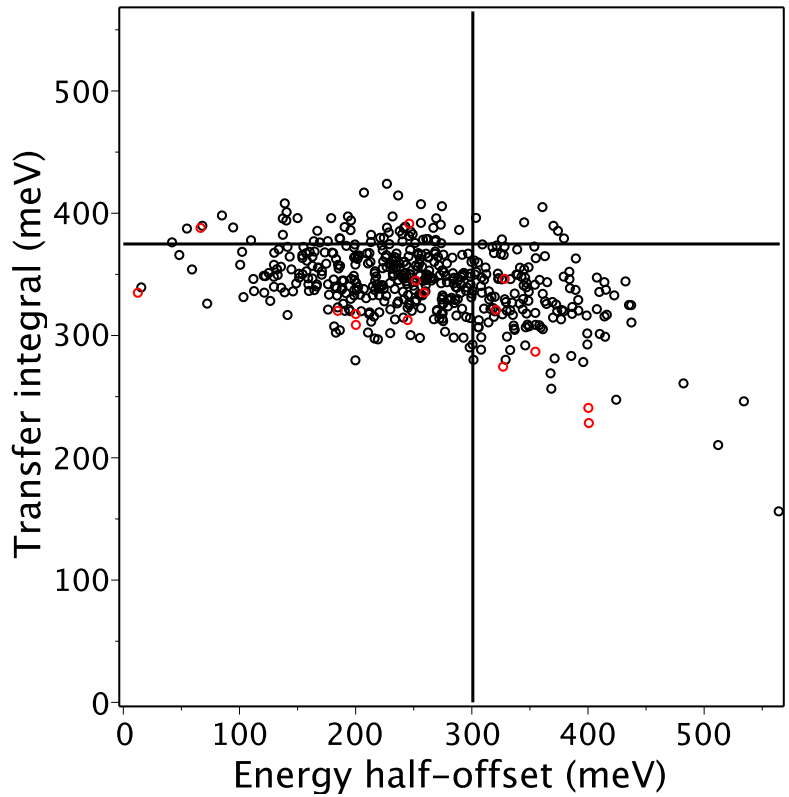
$\Longrightarrow$ 2-LUMO model fails

2-LMO model details: Main disorder is in on-site energies

Fluctuations of half-energy offset and transfer integral in amorphous solid:



(a) Acceptor-acceptor (2-LMO)



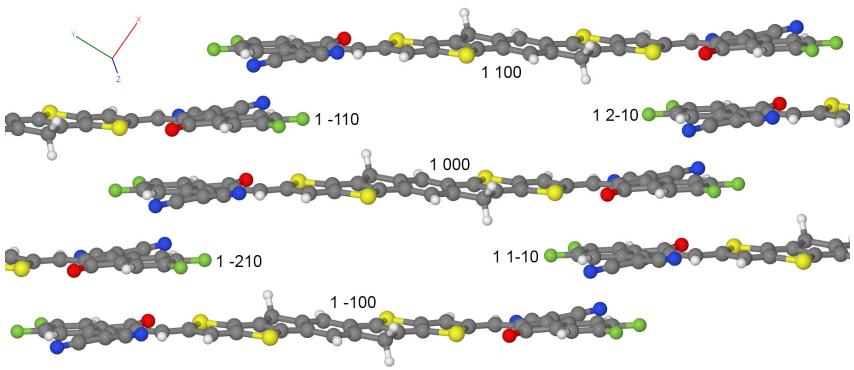
(b) Acceptor-donor (6-LMO)

Result 3/3: Mobility can be underestimated by factor of 2

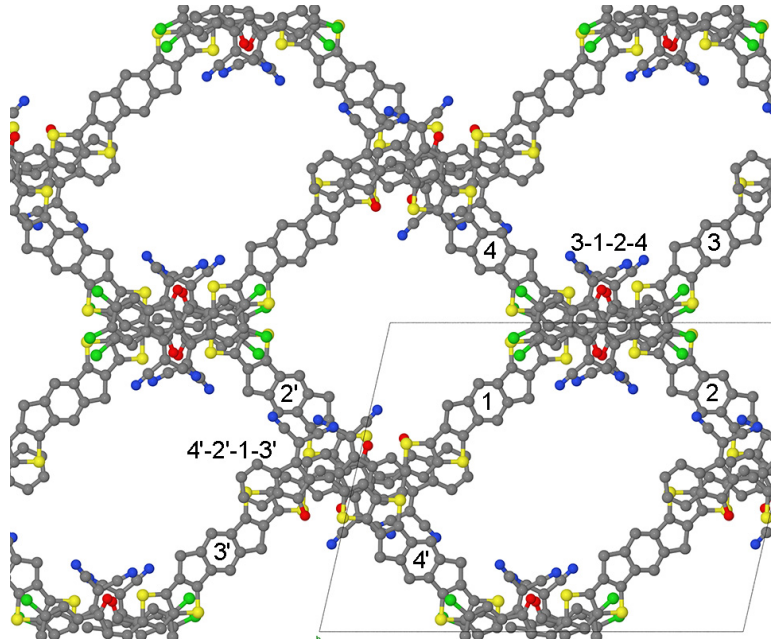
In a solid A-D-A molecules form 2 intermolecular contacts per A

$\Longrightarrow$ coordination number of electronic connectivity graphs is 3

$\Longrightarrow$ either honeycomb (2D) or K4/Laves (3D) lattices



Brickwork packing
(ITIC-4F)



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

Analysis of effective masses and hopping amplitudes (∼mobility) shows that the main effect is that 1-site model underestimates intermolecular couplings by factor of 2

Conclusions

- Electron (as charge carrier) is localized on acceptor block in A-D-A molecules, thus requiring 2-site model for correct description of electronic properties of the conduction band

Appendix

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
   $\Longrightarrow$ CG MOs are usually localized MOs (LMOs)
2. Tight binding parameters ε_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,
  but quality of initial guess (or projector) is important
- Localization to unit cell is performed by Wannier functions
- The largest problem is bands entanglement (e.g. π and σ)
- LMOs can be used to get SCF (MOZYME code in MOPAC,
  fragmentation methods Chem Rev 112, 632 (2012))

Easy to do for small-molecule solids: 'site' = molecule