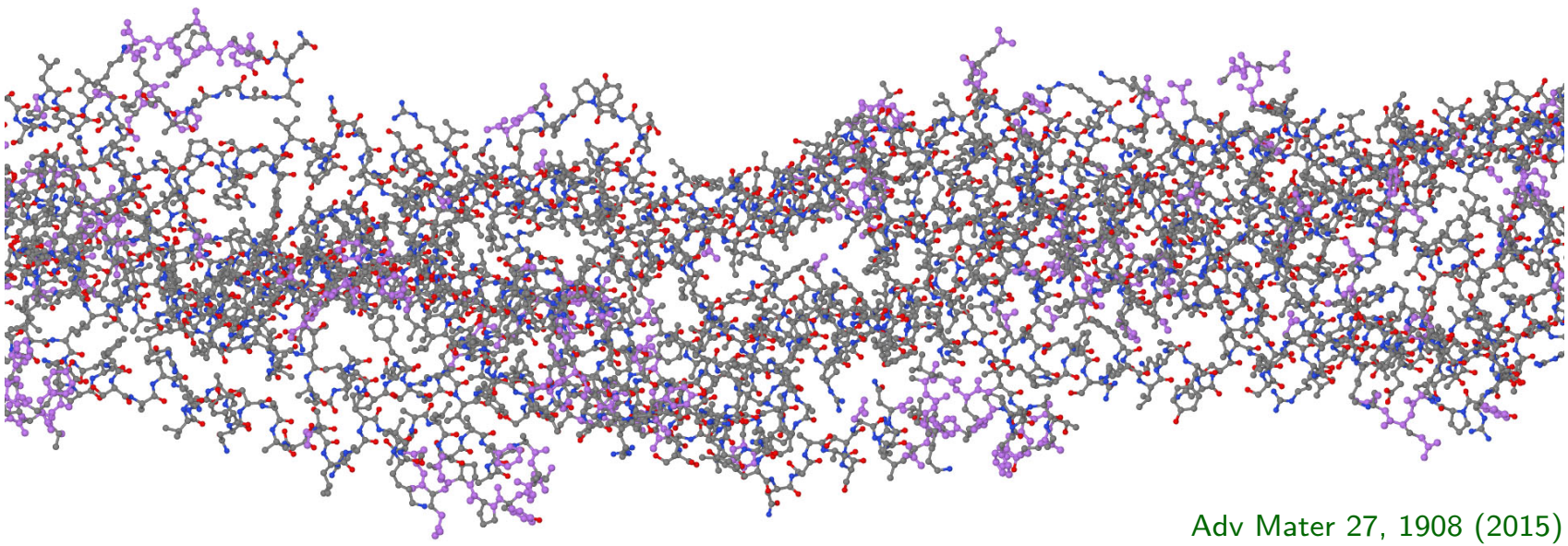
Electronic Coarse-Graining (ECG) in examples

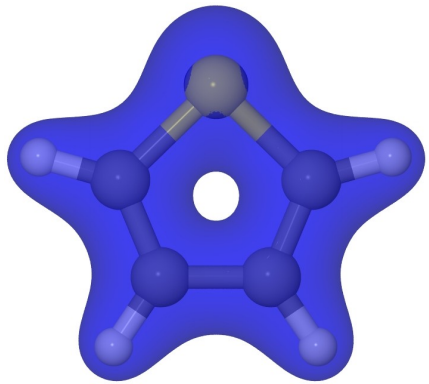
- When do we need ECG? – When system is too complex for use of conventional electronic structure methods (e.g. polymers)
- What is the "price" for ECG? – Only frontier orbitals are calculated (enough for majority of electronic phenomena)
- ECG example 1/4: biopolymers (localized states $\Rightarrow$ trivial ECG)



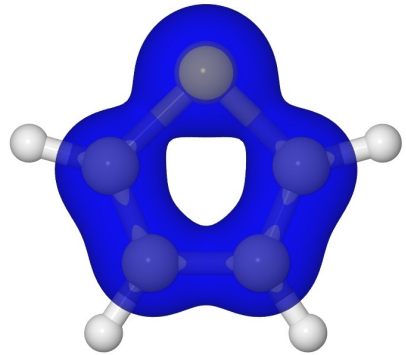
Adv Mater 27, 1908 (2015)

10k non-H atoms $\Longrightarrow$ 50k valence molecular orbitals (MOs) or 1M AOs
but frontier MOs are localized on a small fraction of AOs (violet color)

ECG: more precise formulation



All-electron density



CG density (2 MOs)

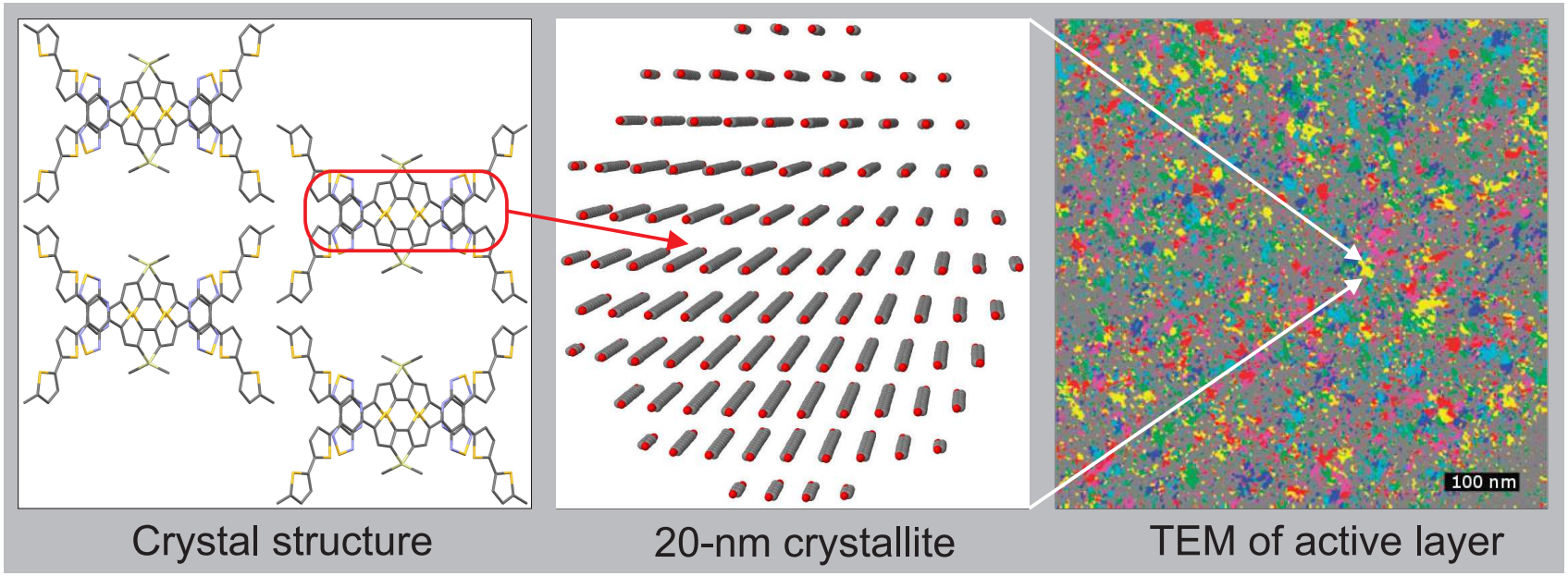
ECG idea/goal: Get minimal basis providing accurate description of a particular electronic property under molecular fluctuations

(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
- Accurate extrapolation to infinite system (if needed)

ECG example 2/4: 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

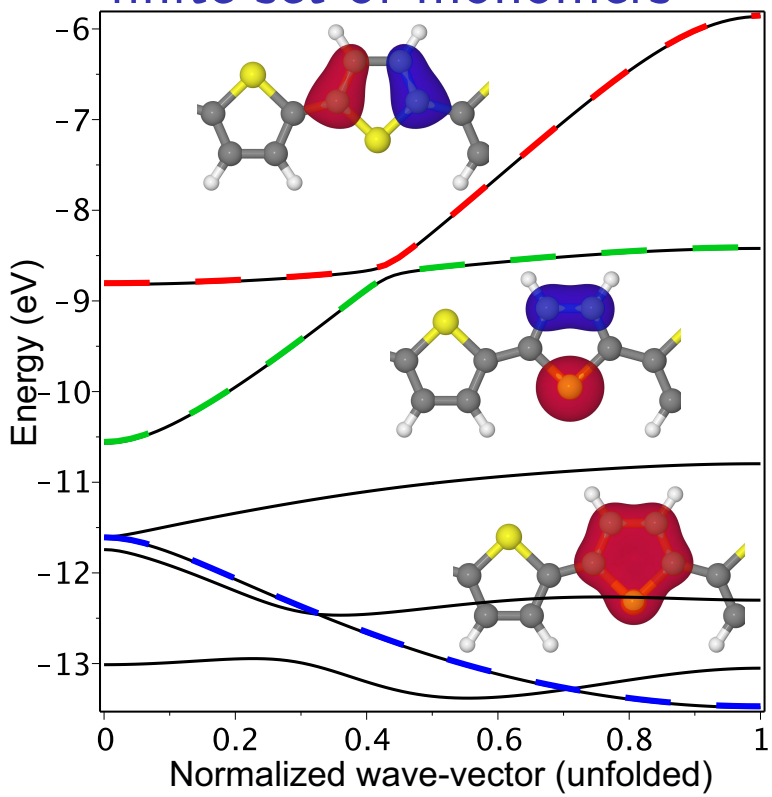
$$\Longrightarrow \sum_{ij} H^{1p}_{ij} c^\dagger_i c_j + \sum_\alpha \hbar\omega_\alpha \left(b^\dagger_\alpha b_\alpha + \frac{1}{2} \right) + \sum_{ij\alpha} \hbar\omega_\alpha g_{ij\alpha} \left(b^\dagger_\alpha + b_\alpha \right) c^\dagger_i c_j$$

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

Annu Rev Phys Chem 66, 305 (2015) first review – Chem Rev 104, 4971 (2004)

ECG in examples 3/4: less trivial coarse-graining

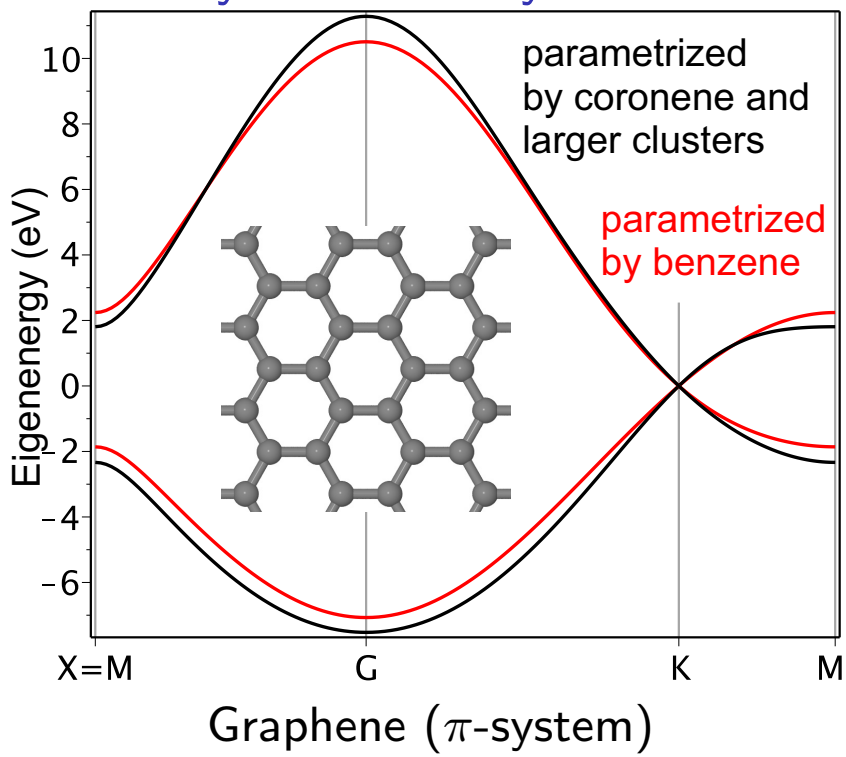
Combinatorial screening of polymers and oligomers from a finite set of monomers



Single polythiophene chain (π-system)

rational design – Chem Sci 8, 1146 (2017), Solar Energy 198, 605 (2020)

Electronic structure of infinite systems with methods available only for finite systems*



Graphene (π-system)

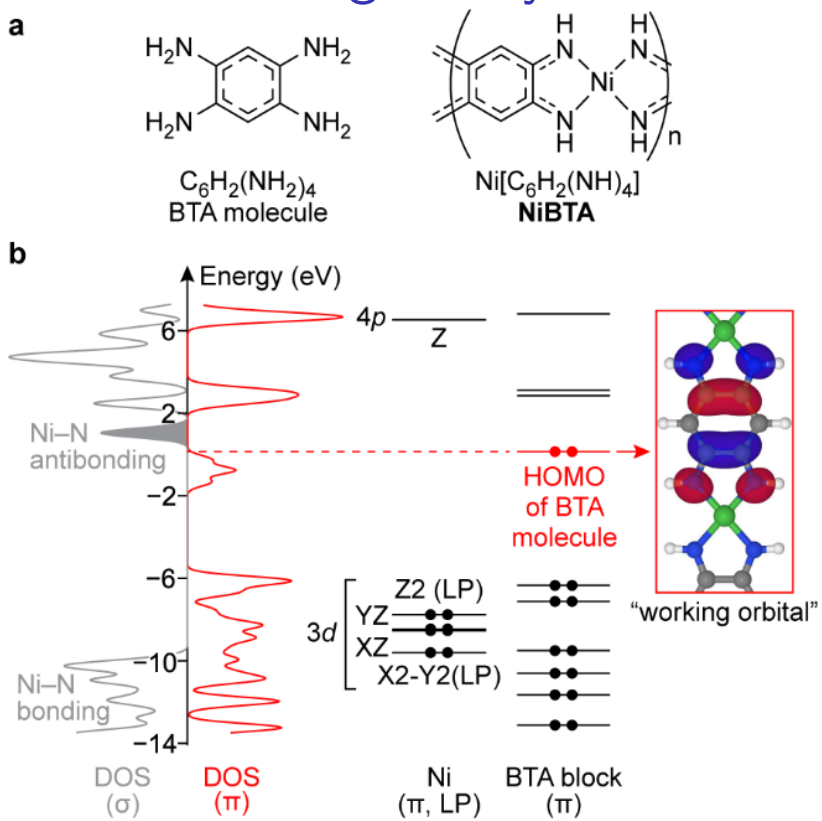
polarons in phosphorene – JPCL 12, 4674 (2021)

*e.g. PBE-D3 is good for crystal structure but bad for e-properties JCTC 19, 8481 (2023)

ECG in examples 4/4: nontrivial coarse-graining

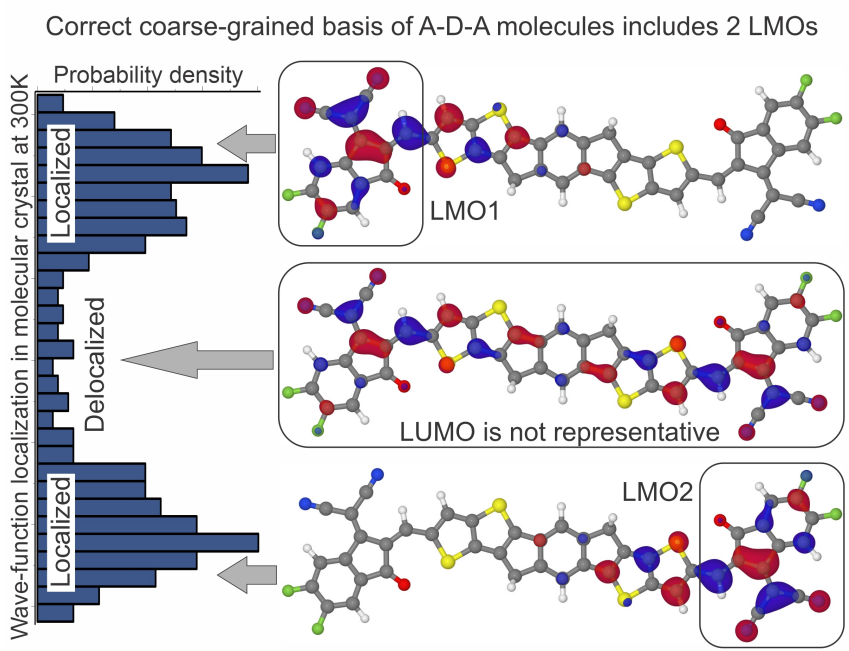
(and applications)

Metal-organic systems



energy storage – Chem Sci 13, 8161 (2022)

Extended molecules



solar cells – JCP 159, 024107 (2023)

... and other structurally complex systems