

Organic Materials for Energy and Optoelectronics

**Lecture on
Modeling of organic semiconductors
for non-theoreticians**

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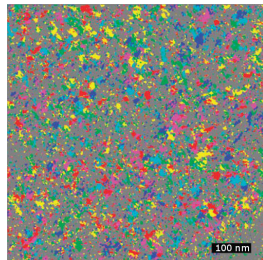
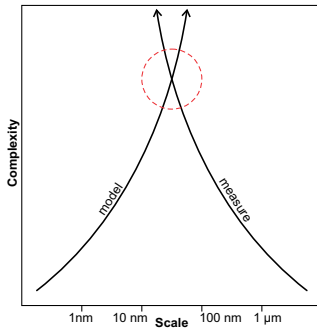
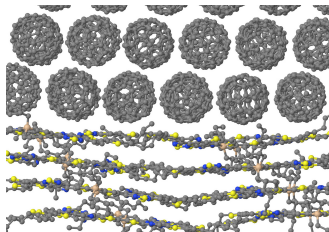
February 18, 2022

Outline

- Introduction
- Overview of approaches
- Illustrative examples

Why modeling is important

Scale gap problem

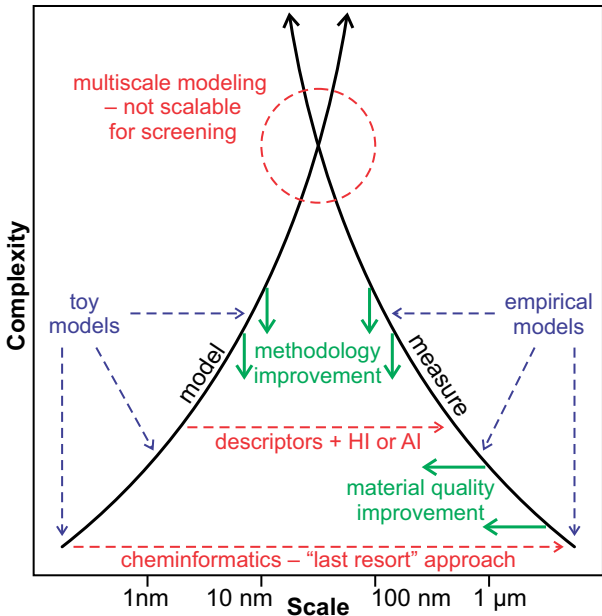


Expected learning outcomes

(for non-theoreticians)

- Ability to communicate with computational materials scientists efficiently and constructively
- Ability to understand computational results (from articles, collaborators, databases), their reliability, and relation to measurements
- Understanding of what can be modeled at what level of accuracy
- Basic knowledge of computational approaches
- Basic skills in analysis of raw computational results (Lab)

Bridging the scale gap



Computational approaches

- First-principle modeling
 - ▶ Coupled clusters
 - ▶ Density functional theory (DFT)
 - ▶ Semiempirical methods
 - ▶ Molecular dynamics with empirical potentials
 - ▶ Multiscale modeling
- Empirical modeling
 - ▶ Kinetic Monte Carlo (KMC)
 - ▶ Continuum models
- Materials data science
 - ▶ Cheminformatics
 - ▶ Descriptors
 - ▶ Machine Learning (ML)

What can be modeled from first principles

(no experimental data are required)

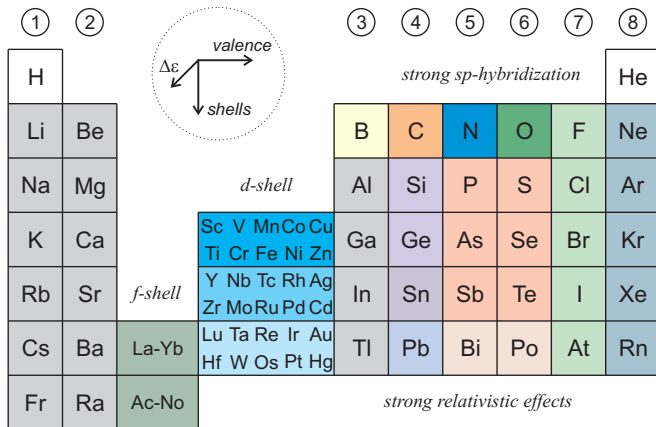
- Almost any property of isolated molecules
(in vacuum or in solution)
- Complex response of simple molecular systems
(e.g. pump-probe)
- Electronic and vibrational spectra, XPS, NMR etc
- Crystal structure, sampling of amorphous structures
- Charge carrier mobility

Questions

1. How many π -orbitals are there per transition metal atom?
2. What if we replace some C atoms by Si and N by P – will we get π -conjugated system?

Why there is a separate lecture on organic materials

Different classes of materials require different approaches



Depends on type of chemical bonding and phenomena of interest

Modeling of organic semiconductors

Challenges vs. opportunities

Main challenges:

- Small band gap – GGA is inaccurate and unreliable
- Soft structure – no harmonic approximation to nuclei dynamics
- Strong electron-phonon coupling[†] – consider nonadiabatic processes
- Complex multiscale morphology (up to 100 nm) – scale gap^{††}
- Complex device structure – multiscale multi-material modeling
- Large repeating unit (10s-100s of atoms) – no high level methods

⇒ *Brute force (material-nonspecific) approach is rarely used*

To model them efficiently one has to take advantage of

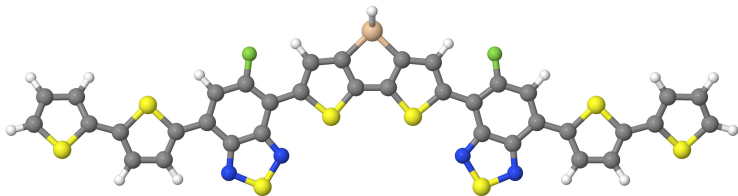
- Only one π -orbital per π -conjugated atom
- Consist of small rigid closed- π -shell blocks
- Light elements – small number of electrons, no SOC
- Heavily benchmarked with multitude of methods
- Fault-free scalable methods exist: CAM-B3LYP-D3/6-31G*

[†] Compared to electronic bandwidth

^{††} What is measured is not what is modeled

Example: molecular solids and polymers

(quasi-1D π -conjugated systems – majority of materials used in organic electronics)



- Have block structure with few interconnections per block
- Each block is rigid, limited number of local structural patterns

⇒ *Success of simple force fields*

- The π -conjugated system of each block is closed-shell
- Inter-block couplings ~ 1 eV \ll band gap of blocks
- Intermolecular couplings ~ 0.1 eV \ll band gap of molecules

⇒ *There must be a set of methods well-tuned for accurate prediction of electronic properties of this class of materials*

Commonly used first-principle methods:

Density functional theory (DFT)

- Best approximation by molecular orbitals (MO)
- Time-dependent DFT (TDDFT) for excited states
- Dispersion-corrected DFT (DFT-D) for vdW interactions
- Functionals:
 - ▶ PBE – avoid except for PBE-D such as PBE-D3
 - ▶ B3LYP – underestimates band gap, dihedrals, ep-couplings
 - ▶ APFD – might be best hybrid (needs more benchmarking)
 - ▶ Range separated hybrids are the most accurate
 - ▶ CAM-B3LYP – safe choice for organic semiconductors
 - ▶ HSE06 – best available for plain waves
- Basis sets
 - ▶ 6-31G* – safe choice for organic semiconductors
 - ▶ Def2-TZVP – for high accuracy

Electronic structure methods are well-benchmarked

Commonly used first-principle methods:

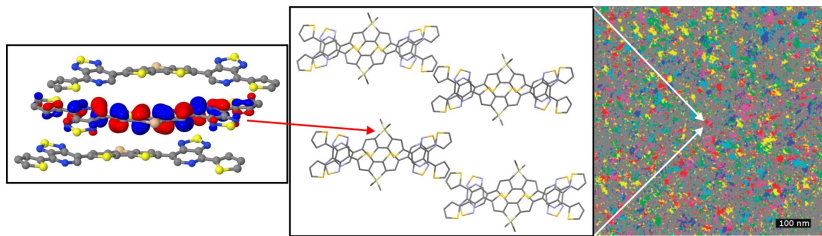
Scalable to thousands of atoms

- Semiempirical – if you need electronic properties
 - ▶ Semiempirical – no accurate parameterization yet
 - ▶ DFTB – very promising but needs to be well parameterized
 - ▶ TB – yes but always requires parameterization
- Empirical potentials – if you do not need electronic properties
 - ▶ Force fields – no accurate parameterization
 - ▶ OPLS – good starting point
 - ▶ ML potentials – under development
- QM+MM – naturally the best (for conjugated systems)

Parameterization is the main problem

First-principles multiscale modeling: bird's eye view

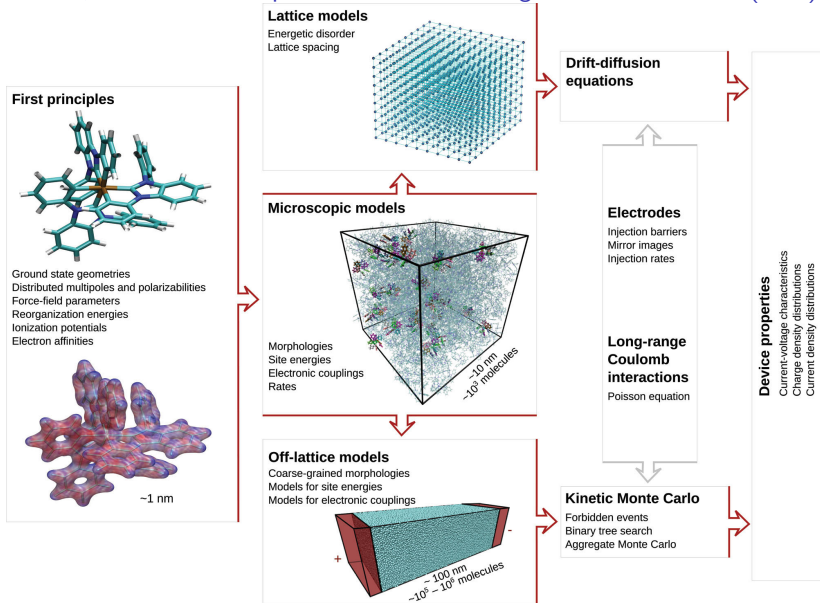
- Combine different approaches on different scales
- Control the accuracy (errors accumulate through the scales)



- Density functional theory on few-molecules scale
- Model Hamiltonian on intermolecular scale
- Molecular mechanics + kinetic equation on mesoscale
- Continuum models on larger scales (diffusion + electrostatics)

Example: fitting statistical models

D Andrienko, Multiscale Concepts in Simulations of Organic Semiconductors (2018)



Another approach: Use descriptors

- Materials stiffness correlates with Young's modulus
- Charge carrier mobility correlates with effective mass
- Ionic conductivity correlates with diffusion barrier
- Battery capacity correlates with metal-ion intercalation energy
- Solar power conversion efficiency correlates with band gap
- Luminescence color correlates with relative dipole moment

Chem Phys 481, 133 (2016)

If many descriptors – use machine learning approaches. The main challenge is to get enough quantity and quality of experimental data. See review Japan J Appl Phys 59, SD0801 (2020)

Questions

1. Suggest descriptors for bulk-heterojunction solar cells.
2. Give examples of π -conjugated systems without scale gap problem.

Structural studies

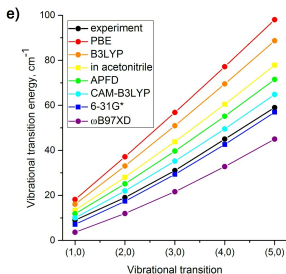
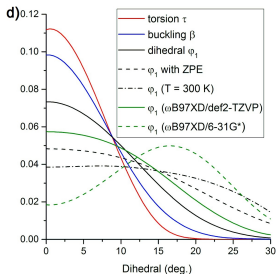
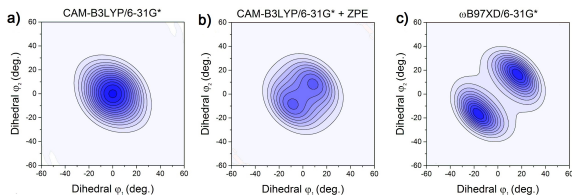
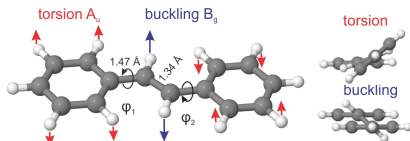
- Refine guessed or measured structure
- Study dependence of structure on parameters
- Establish structure-property relationships
- Predict structure
- Determine or sample conformations and polymorphs

Structural properties sensitive to the method

- Bond Length Alternation (BLA) and dihedrals
- Conformations
- Intermolecular geometry
- Polymorphism

BLA and dihedrals

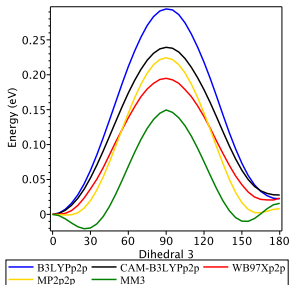
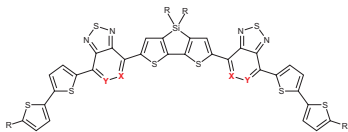
J Phys Chem Lett 10, 3232 (2019)



Highly sensitive to method, multidimensional non-harmonic PES

Conformations: conjugated backbone

J Phys Chem Lett 5, 2700 (2014) Cryst Growth Des 20, 4875 (2020)



method	solv.	1a		3a	
		bb	mol.	bb	mol.
planarized conjugated base					
B3LYP		2		2	
CAM-B3LYP		9		9	
ω B97X		17		17	
MP2		96		...	
MM3		130		251	
dihedrals #3,4 are flipped					
ω B97X		119		38	
MP2		123		...	
CAM-B3LYP		129	128	46	32
B3LYP		132		34	
MM3		132		21	
ω B97X	clf	119		22	
CAM-B3LYP	clf	128	130	33	14
B3LYP	clf	128		19	
dihedrals #1,3,4 are flipped					
ω B97X		147		65	
CAM-B3LYP		159	105	75	98
B3LYP		165		67	
ω B97X	clf	142	242	43	141
CAM-B3LYP	clf	155	102	59	77
B3LYP	clf	158	64	49	-47
saddle point for dihedral #3					
ω B97X		377		169	
CAM-B3LYP		407		209	
B3LYP		468		253	

Table S4. Energies (in meV) of different conformations relative to the energy of the lowest energy conformation: dependence on method. The geometry is fully relaxed from crystalline geometry to local extremum. The default basis set is 6-31g*. Note that conformations with C_2 symmetry is slightly lower in energy than that with σ_h symmetry (typically less than 1 meV difference). Here “bb” means conjugated backbone, “mol.” means the whole molecule. Entries are ordered by the third column (“1a bb”).

Conformations: aliphatic chains

J Phys Chem C 122, 9141 (2018)

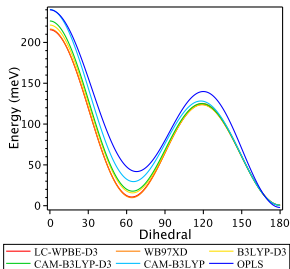
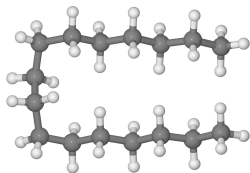


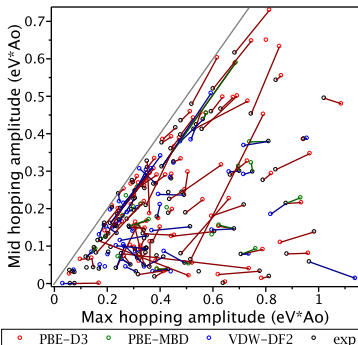
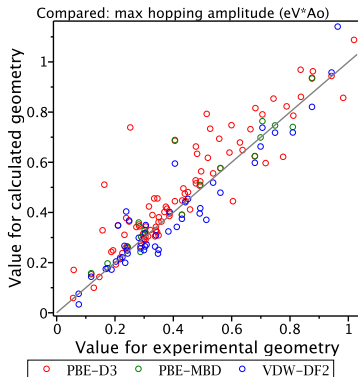
Table S4: Comparison of different methods estimating the relative, hairpin minus trans, energy for a set of polyethylene oligomers (8 to 18 carbons). The geometry is fixed at MP2/cc-pVTZ geometry obtained in Ref.,² except for the last block in the table. The entries correspond to energies in meV. Here σ is RMSD with respect to the reference method which is CCSD(T)/cc-pVTZ.² "Optimized OPLS" means optimized C-C-C dihedral. The supercell size for plane waves is $40 \times 20 \times 20 \text{ \AA}$. See also graphical representation in Fig. S5.

	σ	8	10	12	14	16	18
Reference data							
CCSD-T/cc-pVTZ	0	65	52	37	5	-30	-73
6-311G*							
CAM-B3LYP-D3	5	71	61	42	10	-30	-72
B3LYP-D3	16	60	50	31	-12	-53	-98
vdW-DF2	19	90	83	62	14	-31	-71
PBE-MBD	22	66	55	34	-21	-62	-108
LC-wPBE-D3	50	29	15	-5	-47	-88	-140
wB97XD	90	24	11	-10	-95	-145	-215
CAM-B3LYP	195	138	143	148	227	222	227
6-311+G(3df,2p)							
CAM-B3LYP-D3	10	78	67	49	7	-33	-75
B3LYP-D3	21	65	54	36	-20	-61	-106
LC-wPBE-D3	39	41	29	10	-39	-77	-127
wB97XD	84	33	20	1	-90	-138	-207
CAM-B3LYP-D3							
6-311G*	5	71	61	42	10	-30	-72
6-311G**	8	68	57	38	-2	-43	-86
6-311+G(3df,2p)	10	78	67	49	7	-33	-75
6-311G(2d,p)	10	78	68	49	9	-30	-72
6-311+G(2d,p)	14	82	72	54	16	-23	-65
6-31G(2d,p)	18	73	61	37	-11	-56	-103
6-31G*	19	66	56	33	-12	-58	-104
6-31G**	20	67	57	34	-14	-59	-106
6-31+G(2d,p)	29	94	84	67	34	-4	-45
Geometry relaxed with the same method							
CAM-B3LYP-D3	4	67	57	38	4	-36	-79
optimized OPLS	8	54	41	27	3	-34	-72
B3LYP-D3	18	56	45	25	-14	-55	-100
LC-wPBE-D3	51	28	15	-6	-49	-88	-141
wB97XD	96	21	8	-13	-103	-154	-223
OPLS	118	160	161	149	135	97	58
CAM-B3LYPp3p	128	127	129	128	128	128	128

Intermolecular geometry

Tested here is product of electronic coupling and hopping distance

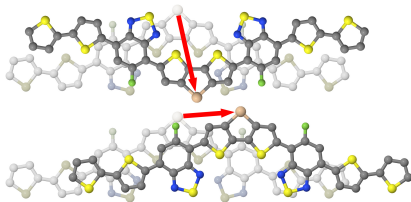
Test set: > 50 crystals, including all high- μ from Chem Soc Rev 47, 422 (2018)



Polymorphism of molecular crystals

Sci Adv 5, eaau3338 (2019)

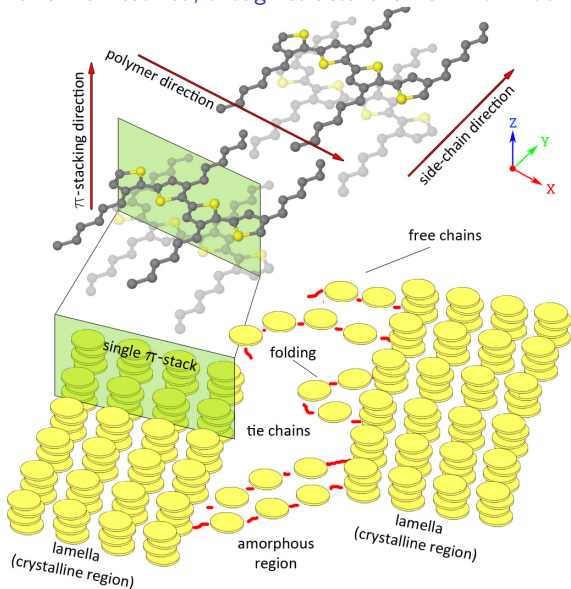
- DFT-D correctly predicts relative energy of polymorphs for small-molecule crystals (TCNQ, indigo, rubrene)
- Force fields can be used for prescreening (MM3 in *J Phys Chem Lett* 5, 2700 (2014), OPLS in *J Phys Chem C* 122, 9141 (2018))
- For large molecules with aliphatic chains kinetic and entropic factors might be essential



DFT-D predicts that antiparallel stacking is 0.18 eV/mol lower in energy than the observed parallel stacking
Adv Funct Mater 28, 1702073 (2017)

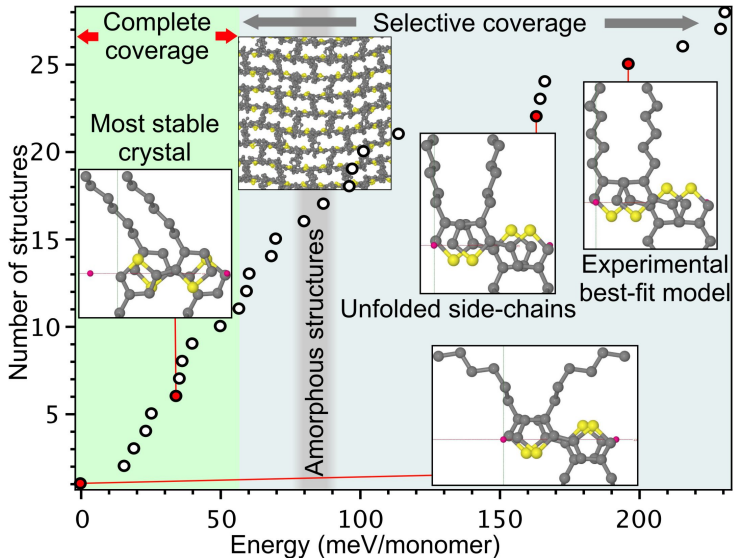
Polymorphism of bulk polymers: example of P3HT

Atomic positions remain unresolved, though structure is well known down to nanometers



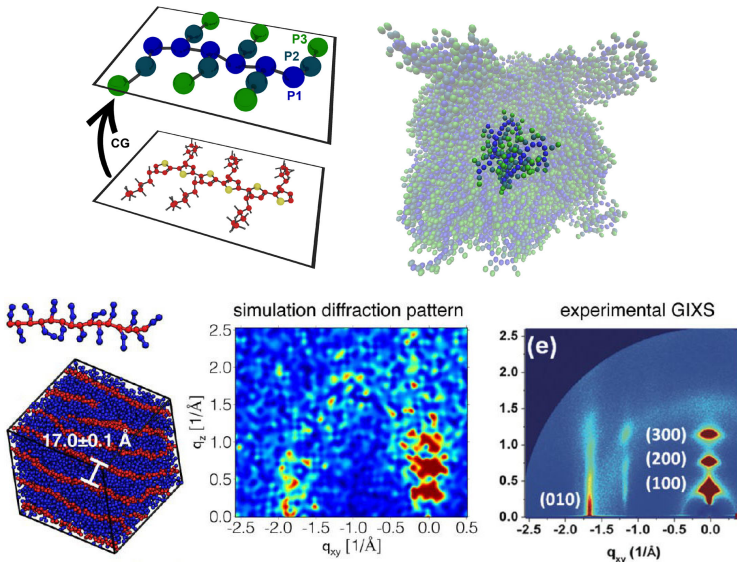
Polymorphism of bulk polymers: example of P3HT

J Phys Chem C 122, 9141 (2018)



Example: coarse-graining molecular degrees of freedom

M L Jones, E Jankowski, Molec Simul 43, 756 (2017)



Electronic properties

- Wave-function
- Effective mass
- HOMO/LUMO energies, IP/EA, charge gap
- Optical gap and excitations
- Intermolecular couplings
- Small-gap systems

Electronic properties not sensitive to the method

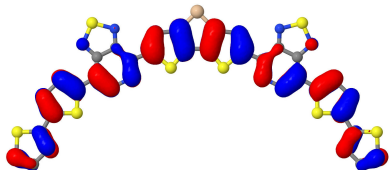
- Wave-function
- Intraband properties (e.g. effective mass)

Systematic trends with HF content \implies use "bracketing" & IP-tuning

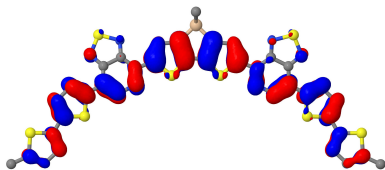
PBE(0) – B3LYP(.2) – HSE06(.25/0), APF(.23), PBE0(.25) –
– CAM-B3LYP(.19/.65) – ω B97X(.16/1)

Wave-function

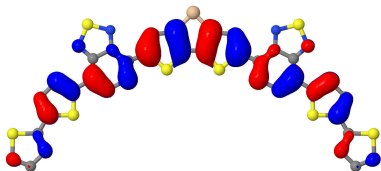
(not sensitive to the method)



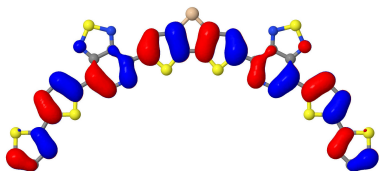
HOMO (CAM-B3LYP)



HOMO (PM6)



hole NO (CAM-B3LYP)



hole NO (B3LYP)

Wave-function follows BLA pattern, e.g. HOMO is on double bonds

Effective mass

(not very sensitive to the method)

Effective mass for holes in trans-polyacetylene:

- 0.074 – PBE
- 0.076 – HSE06
- 0.076 – B3LYP
- 0.090 – CAM-B3LYP
- 0.097 – ω B97X

Because of narrow complex-shaped bands, other intraband parameters such as bandwidths are often more informative than effective masses

HOMO/LUMO energies and IP/EA

Theoretical definitions

- Ionization Potential, $IP = E(N - 1) - E(N) > 0$
- Electron Affinity, $EA = E(N) - E(N + 1)$ (usually positive)
- Charge gap = $IP - EA$
- Absolute electronegativity = $(IP + EA)/2$
- Vertical IP/EA – geometry fixed at relaxed initial state
- Adiabatic IP/EA – fully relaxed geometries

Experimental determination for organic semiconductors

- Cyclic voltammetry (adiabatic)
- Photoemission spectroscopy (vertical, VDE instead of EA)

Terminology convention: Experimentalists do not use IP/EA terminology, but use HOMO/LUMO energies instead. For bulk 3D systems this gives an intrinsic property, but for systems exposed to an environment, IP/EA strongly depend on the environment.

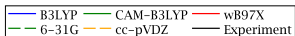
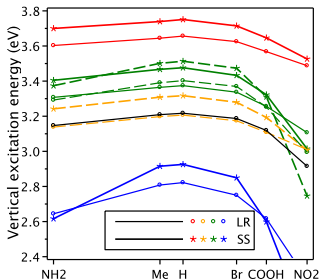
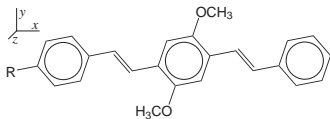
Calculation of IP/EA

- Molecules – by definition
 - ▶ Small molecules – see JCTC 12, 595;605;615;627 (2016)
- Molecular solids
 - ▶ as molecule in a dielectric medium
 - ▶ as solid in PBC – see below
- Extended π -conjugated systems
 - ▶ use HOMO/LUMO (+GW)
 - ▶ extrapolate PRB 92, 195134 (2015)
- Relative IP/EA in same conditions – use HOMO/LUMO

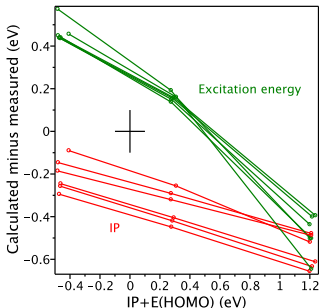
Koopman's theorem and IP-tuning

Chem Phys 481, 133 (2016) JCTC 12, 605 (2016); Acc Chem Res 47, 2592 (2014)

- Use $IP + E_{HOMO} = 0$ to select best functional or tune its parameters
- Useless for small molecules, but works well for larger ones



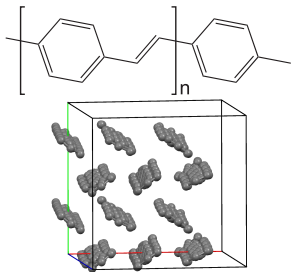
functional	$IP + E_{HOMO}$ (eV)
B3LYP	+1.2
CAM-B3LYP	+0.3
ω B97X	-0.4



Optical gap and excitations

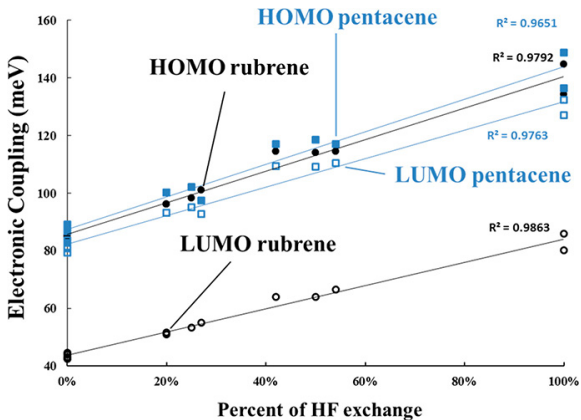
- Molecules – by TDDFT or GW(+BSE)
- Molecular solids, multimers – vibronic effects are important
- Extended π -conjugated systems – as solid in PBC
- Relative gap in same conditions – use HOMO-LUMO gap

	bandgap (eV)	
	crystal	polymer
wB97X	5.9	6.6
CAM-B3LYP	4.4	4.8
experiment	3.5	–
B3LYP	2.2	2.5
HSE06	1.7	2.1
PBE	1.1	1.3



Intermolecular couplings

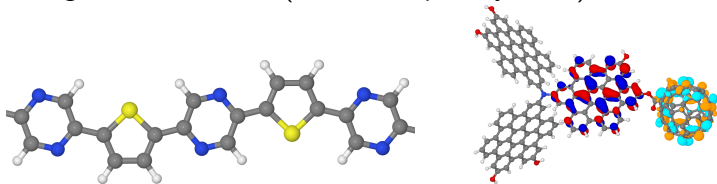
J Phys Chem Lett 4, 919 (2013)



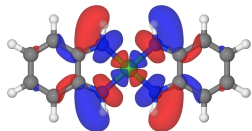
Small-gap systems

(very sensitive to the method)

- Charge transfer states (donor-acceptor systems) – use DFT



- Spin-degenerate cases (transition metals) – use DFT with care



- Strongly correlated systems (extended π -conjugation)
— see example of acenes *J Chem Phys* 148, 134112 (2018)

Spectroscopy

— primary experimental characterization tool for organic semiconductors

- Vibronic couplings for a single electronic state
- UV-Vis spectra
- Raman spectra
- Other optical: IR, photoemission, pump-probe . . .
- Also nonoptical: XPS, NMR . . .

Vibronic effects important, they are very sensitive to method

Vibronic couplings for a single electronic state

Independent boson model = Displaced harmonic oscillator model – exactly solvable

The key assumption is that separation between electronic states is larger than vibronic bandwidth \implies

$$H = \varepsilon n + \sum_{\alpha} \hbar \omega_{\alpha} \left(b_{\alpha}^{\dagger} b_{\alpha} + \frac{1}{2} \right) + \sum_{\alpha} \hbar \omega_{\alpha} g_{\alpha} \left(b_{\alpha}^{\dagger} + b_{\alpha} \right) n$$

here ε – electronic level, b_{α} – normal modes, g_{α} – vibronic (electron-phonon) couplings, $S_{\alpha} = g_{\alpha}^2$ – Huang–Rhys factors

Solution:

$$\tilde{H} = e^P H e^{-P} = (\varepsilon - \lambda) n + \sum_{\alpha} \hbar \omega_{\alpha} \left(b_{\alpha}^{\dagger} b_{\alpha} + \frac{1}{2} \right)$$

where *displacement operator* and *electronic state relaxation energy*

$$P = n \sum_{\alpha} g_{\alpha} \left(b_{\alpha} - b_{\alpha}^{\dagger} \right), \quad \lambda = \sum_{\alpha} \hbar \omega_{\alpha} g_{\alpha}^2$$

Vibrationally resolved spectra: transition spectral density

Absorption/emission intensity:

$$I_{\text{emi}}(E) = \frac{4E^3}{3\hbar^4 c^3} |d|^2 \sigma^{\text{excited}}(-E), \quad I_{\text{abs}}(E) = \frac{4\pi^2 E}{3\hbar c} |d|^2 \sigma^{\text{ground}}(E)$$

Transition spectral density:

$$\sigma(E) = \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} \hat{\sigma}(t) e^{itE/\hbar} dt$$

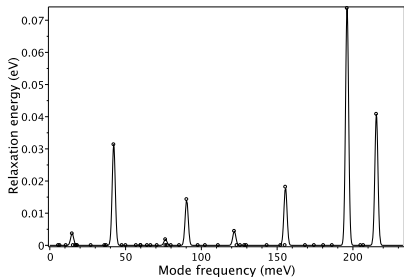
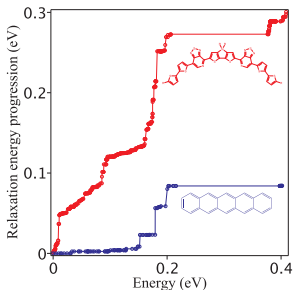
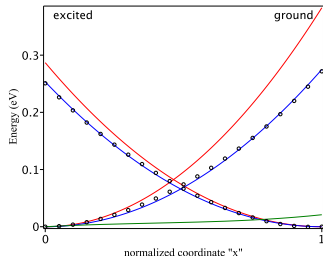
where the phonon correlator

$$\hat{\sigma}(t) = \exp \left[\sum_{\alpha} S_{\alpha} \coth \frac{\hbar\omega_{\alpha}}{2T} (\cos \omega_{\alpha} t - 1) - i \sum_{\alpha} S_{\alpha} \sin \omega_{\alpha} t - i \frac{E_{00} + \lambda'}{\hbar} t - \frac{\sigma^2 + 2\lambda' T}{2\hbar^2} t^2 \right]$$

here λ' is reorganization energy due to classical modes and σ^2 is an inhomogeneous broadening

Calculating vibronic couplings

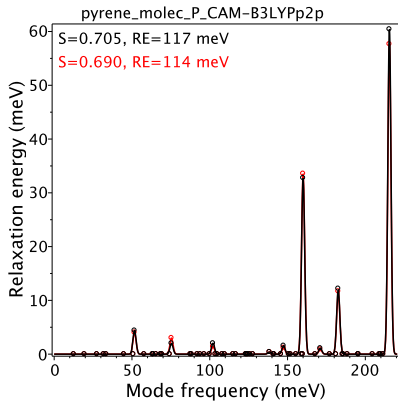
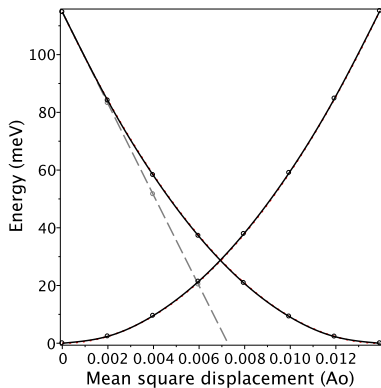
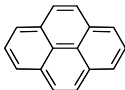
- Get two relaxed geometries: for zero and one quasiparticle at site
- Project atomic displacement onto normal modes ξ_α , then $g_\alpha = -\frac{\xi_\alpha^{(0)}}{\sqrt{2}}$
- Rescale g and ω for weak anharmonic effects



$$\lambda(E) = \sum_{\hbar\omega_\alpha < E} g_\alpha^2 \hbar\omega_\alpha$$

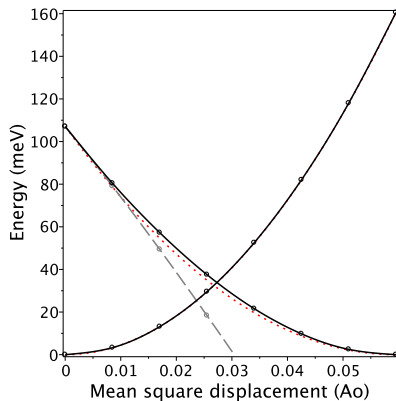
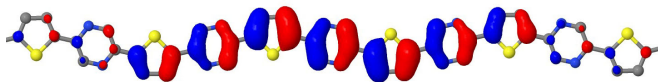
Accuracy of displaced harmonic oscillator approximation

Pyrene molecule – ideal case: curves are symmetric and harmonic, gradient can be used



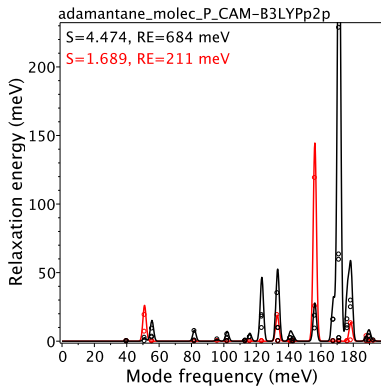
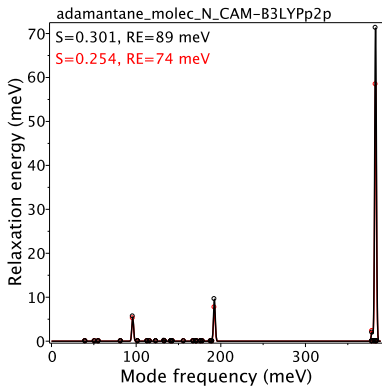
Accuracy of displaced harmonic oscillator approximation

Long oligomer – works satisfactory but there is asymmetry and some anharmonicity



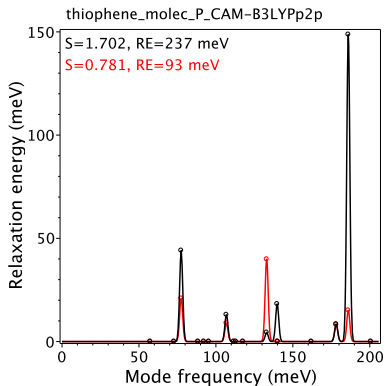
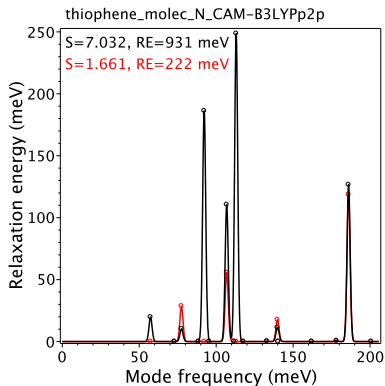
Accuracy of displaced harmonic oscillator approximation

Adamantane – anion is OK, cation is unsatisfactory – degenerate HOMO



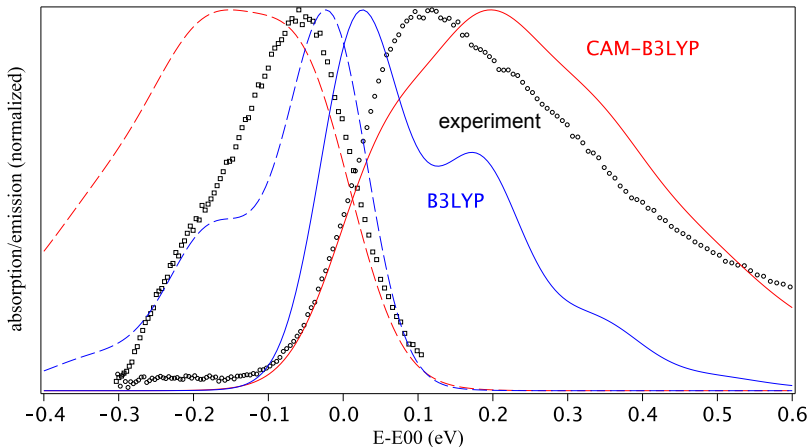
Accuracy of displaced harmonic oscillator approximation

Thiophene – unsatisfactory – anharmonic PES



Vibrationally resolved UV-Vis spectra: example

Annu Rev Phys Chem 66, 305 (2015)



B3LYP underestimates vibronic couplings for low- ω modes
CAM-B3LYP overestimates vib. couplings for high- ω modes

Vibrationally resolved UV-Vis spectra: low-T example

J Chem Phys 116, 8569 (2002)

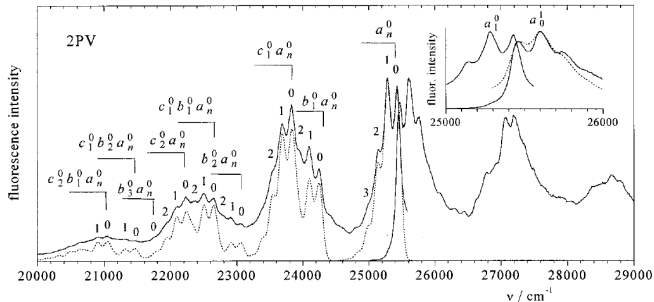
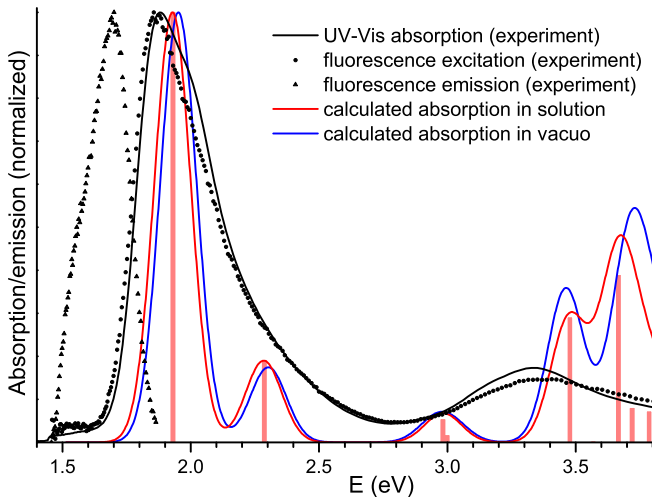


FIG. 7. Fluorescence excitation spectrum (right) and fluorescence emission spectrum (left) of 2PV in tetradecane at 15 K. Solid line: experiment; dashed line: simulation according to Eq. (1) with three modes ($\nu_a = 150 \text{ cm}^{-1}$, $\nu_b = 1200 \text{ cm}^{-1}$, $\nu_c = 1600 \text{ cm}^{-1}$, $S_a = 1.05$, $S_b = 0.45$, $S_c = 0.67$, $\gamma = 130 \text{ cm}^{-1}$). Inset: Region of the electronic origin; dashed line: simulation of the fluorescence excitation spectrum according to Eq. (10) with $T = 15 \text{ K}$, $D = 5.5$.

UV-Vis spectra: multiple electronic transitions

J Phys Chem C 117, 4920 (2013)



Observe non-gaussian structure of the main absorption band

Raman spectra

- Off-resonant Raman activities can be calculated by DFPT, e.g. available in Gaussian as a black-box solution
- In experiment usually resonant Raman spectra are measured
- Resonant Raman intensities can be calculated by

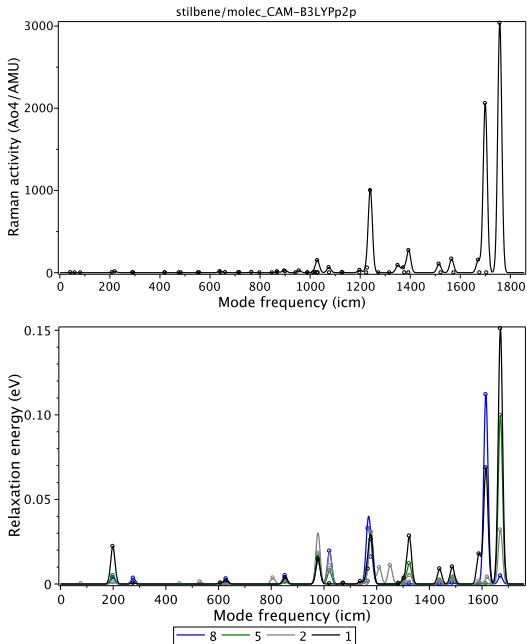
$$I_{\omega} \sim \lambda \omega^n d^4 / \Delta \Omega^2$$

where d is transition dipole moment, $\Delta \Omega$ is deviation from resonance, and n together with normalization factor depend on details of experiment

[J McHale, Molecular Spectroscopy (CRC, 2017)]

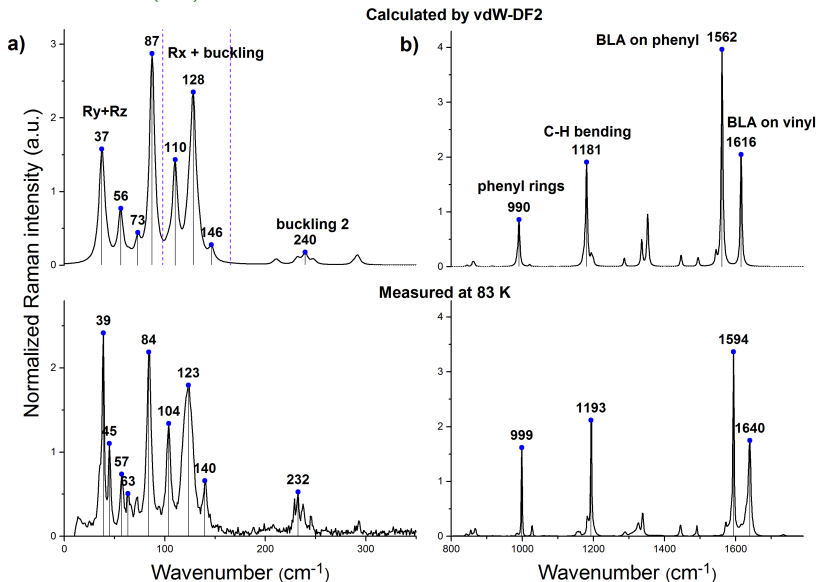
- The main challenge is to calculate vibronic couplings to higher excitations

Raman spectra of stilbene molecule



Raman spectra of stilbene crystal

J Phys Chem Lett 10, 3232 (2019)



Energy and charge transport

- Brute force approach – nonadiabatic MD – not scalable
- Simplified scalable approach – most commonly used
- Beyond the simplified approach – ideas

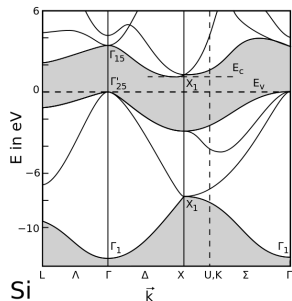
Multiple scales: how to approach

Scale	Method	Electronic processes
molecular complex (1000 atoms)	NAMD	intramolecular relaxation internal conversion intermolecular transfer redox reactions
single bulk phase (crystal,amorphous)	MF	intraband relaxation charge carrier scattering
mesoscale (up to continuum)	KMC MD ??	hopping ionic transport electronic + ionic
device	PDE	diffusive transport

Challenge: no black-box tools, it is complex problem (combine different approaches on different scales, error accumulation through scales)

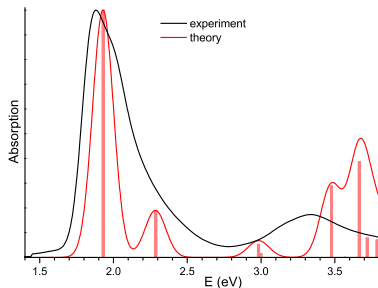
NAMD=nonadiabatic MD, MF=mean field, KMC=kinetic Monte Carlo, MD=molecular dynamics, PDE=partial differential equations

Some definitions: electronic and vibronic bandwidth



Electronic bandwidth

$$W_{\text{el}}^2 = \langle \Delta \varepsilon^2 \rangle + \langle \Delta \varepsilon^2 \rangle_T$$



Vibronic bandwidth

$$W_{\text{vib}}^2 = \sum_{\alpha} g_{\alpha}^2 \hbar^2 \omega_{\alpha}^2 \coth \frac{\hbar \omega_{\alpha}}{2T}$$

For bandwidth W , correlation function decreases as $e^{-W^2 t^2 / 2\hbar^2}$ at small t

Electron-phonon couplings: organic vs inorganic

Electron-phonon couplings are always large for bonding electrons, with W_{vib} of the order of tenths of eV. The difference is in W_{el} :

“Inorganic electronics”

$$W_{\text{el}} \gg W_{\text{vib}}$$

(weak el-ph correlations)

\implies model of free charge carriers scattered by phonons

“Organic electronics”

$$W_{\text{el}} \sim W_{\text{vib}}$$

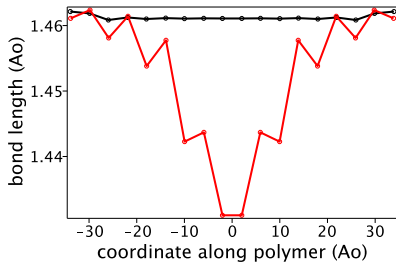
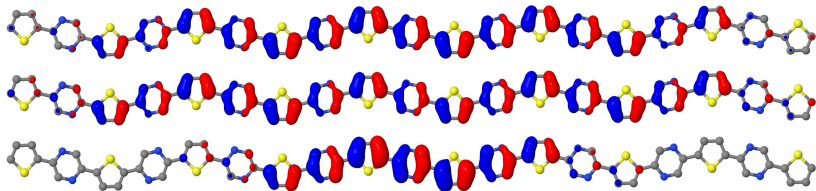
(strong el-ph correlations)

\implies more complicated models

Additional complication: soft lattice (no rigid framework, flexible dihedrals, intermolecular motions) \implies doping and intercalation challenges (also chalcogenides, transition metal oxides)

Polaron formation

(HOMO, cation NO, polaron NO)



Charge carrier mobility

Basic equations in homogeneous medium

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

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

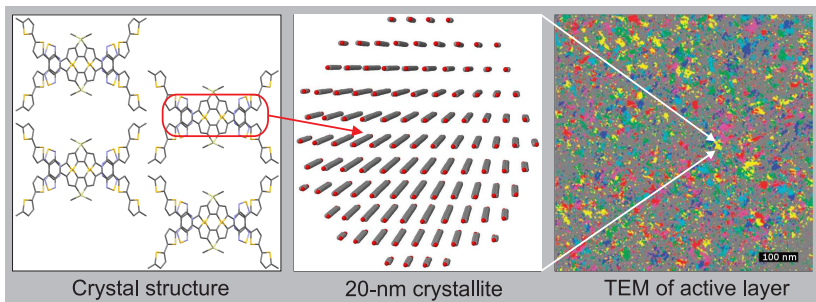
* Purely **electronic** and **electron-phonon** interaction terms are factorized

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 = $\sqrt{D \cdot \text{lifetime}}$

Simplified approach for a molecular solid



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

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

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

Holstein–Peierls Hamiltonian

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

here c_i – quasiparticles (excitons, holes etc.) described by coarse-grained Hamiltonian, b_{α} – normal modes or phonons,

$$H_{ij}^{1p} = \delta_{ij} \varepsilon_i + (1 - \delta_{ij}) t_{ij},$$

ε_i – onsite energy, t_{ij} – transfer integral, $g_{ij\alpha}$ – electron-phonon coupling (local for $i = j$, nonlocal otherwise)

Approximations:

- mean field approximation for electrons (one may add interaction terms)
- harmonic approximation for atomic motion (essential for quantum modes)
- linear electron-phonon coupling

For calculation of nonlocal (intermolecular) couplings see [Phys Stat Sol B 248, 511]

Calculating coarse-grained electronic Hamiltonian

See also [Chem Rev 117, 10319 (2017)]

Definition: For all possible atomic configurations, the lowest eigenvalue of H^{1p} should match the exact electronic energy

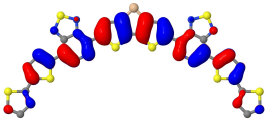
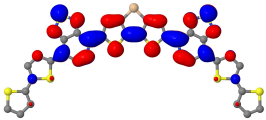
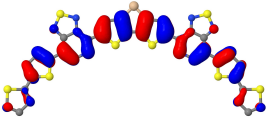
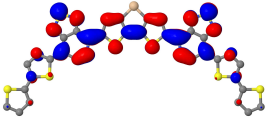
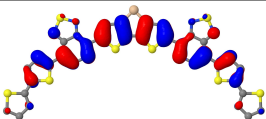
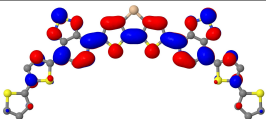
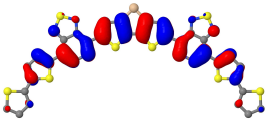
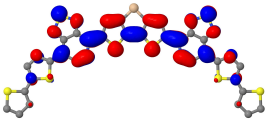
Dimer approximation:

- Frenkel excitons: from excitations energies and transition dipoles [J Phys Chem C 117, 4920]
- Electrons/holes: from DFT Fock matrices [JPCC 117, 4920] (HOMO/LUMO=hole/electron, HOMO×LUMO=exciton)
- Semiempirical approaches [Int J Q Chem 108, 51; JACS 127, 4744]

Hole=HOMO, electron=LUMO, exciton=HOMO×LUMO

	HOMO	LUMO
ground state $n_h = 2$ $n_e = 0$		
	hole NO	electron NO
cation/anion $n_{h/e} = 1$ $\Delta n_2 = .07/.06$		
singlet exciton $n_h = 1 + .12$ $n_e = 1 - .12$		
triplet exciton $n_h = 1 + .17$ $n_e = 1 - .18$		

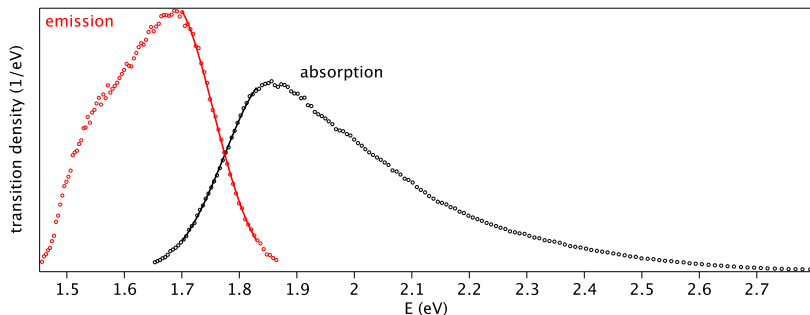
Excitation=exciton

	hole NTO/NO	electron NTO/NO
singlet exciton $n_h = 1 + .12$ $n_e = 1 - .12$		
singlet transition $n_{h/e} = 1 \pm .17$		
triplet exciton $n_h = 1 + .17$ $n_e = 1 - .18$		
triplet transition $n_{h/e} = 1 \pm .25$		

Solving Holstein–Peierls Hamiltonian: hopping regime

Calculate hopping rates using Fermi's golden rule:

$$w_{(i \rightarrow j)} = \frac{2\pi}{\hbar} |t_{ij}|^2 J_{ij}, \quad J_{ij} = \int \rho_i^{\text{emi}}(E) \rho_j^{\text{abs}}(E) dE \text{ is spectral overlap}$$



Details: charge/energy transfer in donor-acceptor model

(two-site Holstein model by perturbation theory in inter-site electronic coupling)

Fermi's golden rule:

$$w = \frac{2\pi}{\hbar} \sum_{nn'} \rho_n |H_{nn'}^{\text{int}}|^2 \delta(E_{nn'}), \quad E_{nn'} = E_{n'} - E_n,$$

where ρ_n is initial population and δ is spectral lineshape function.
For local electron-phonon couplings (Holstein model)

$$H_{nn'}^{\text{int}} = t \langle n_{\text{D}} | n'_{\text{D}} \rangle \langle n_{\text{A}} | n'_{\text{A}} \rangle, \quad \rho_n = \rho_{n_{\text{D}}}^{\text{D}} \rho_{n_{\text{A}}}^{\text{A}}, \quad E_n = E_{n_{\text{D}}} + E_{n_{\text{A}}},$$

where $n_{\text{D/A}}$ ($n'_{\text{D/A}}$) denotes initial (final) state of donor/acceptor
and vibrational overlaps $\langle n | n' \rangle$ are called Franck–Condon factors.

$$\implies w = \frac{2\pi}{\hbar} |t|^2 J, \quad \text{where}$$

$$J = \int \sigma^{\text{D}}(-E) \sigma^{\text{A}}(E) dE \quad \text{is spectral overlap}$$

$$\sigma(E) = \sum_{nn'} \rho_n \langle n | n' \rangle^2 \delta(E - E_{nn'}) \quad \text{is transition spectral density,}$$

whose Fourier transform is correlator between initial and final states.

Spectral overlap via phonon correlator

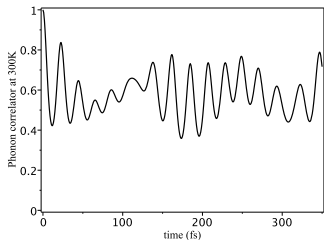
$$J_{ij} = \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} \left\langle e^{itH_i^{\text{vib}}/\hbar} e^{-itH_j^{\text{vib}}/\hbar} \right\rangle dt$$

Independent boson model (displaced harmonic oscillator):

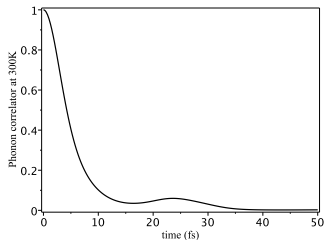
$$J_{ij} = \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} \hat{\delta}(t) e^{-i\omega_{00}t} \prod_{\alpha} C_{\alpha}(t) dt,$$

where $C_{\alpha}(t) = \exp \left[g_{\alpha}^2 \left(\coth \frac{\hbar\omega_{\alpha}}{2T} (\cos \omega_{\alpha}t - 1) - i \sin \omega_{\alpha}t \right) \right]$,
 $\hbar\omega_{00}$ is 0-0 transition energy,

$\hat{\delta}$ is line shape function (inhomogeneous broadening) e.g. $e^{-\sigma^2 t^2/2\hbar^2}$



rigid vs. soft
molecule

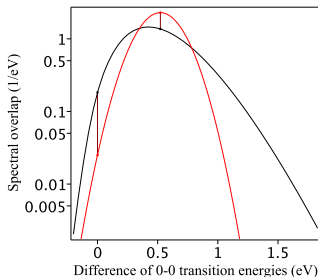
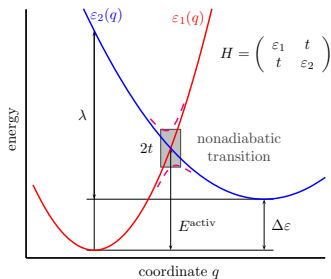


Spectral overlap in high temperature limit: Marcus formula

If $T \gg \hbar\omega$ then

$$J_{ij} = \frac{1}{\sqrt{4\pi\lambda T}} \exp \left[-\frac{(\lambda + \varepsilon_j - \varepsilon_i)^2}{4\lambda T} \right],$$

where $\lambda = E_i^{\text{polaron}} + E_j^{\text{polaron}}$ is the reorganization energy



— independent boson model — Marcus formula

Final step: solving master equation for hopping

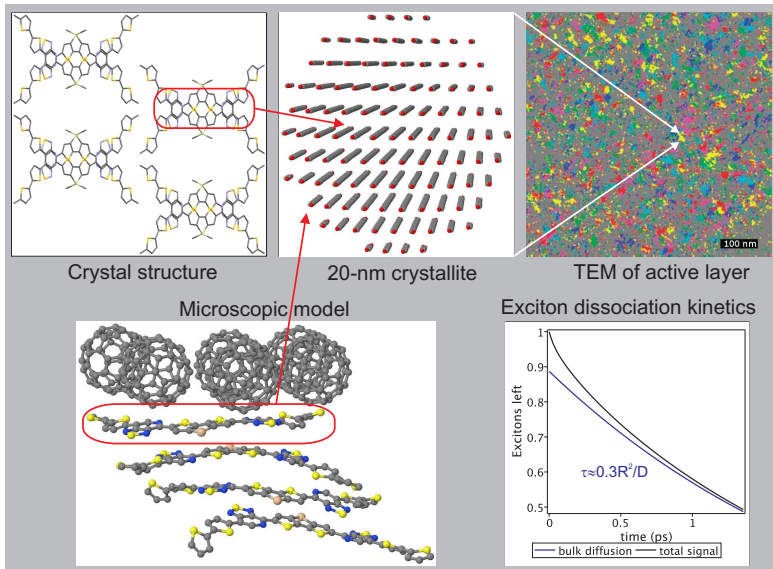
Master equation for average site occupation $n_i(t)$:

$$\frac{dn_i}{dt} = \sum_j (n_j w_{ji} - n_i w_{ij})$$

Kinetic Monte Carlo (KMC) or direct solution?

- Use direct formulas whenever is possible, see [JPCC 117, 4920]
- If system size is too large for matrix methods or if the problem is nonlinear use KMC

Example: Modeling exciton dissociation



In absence of traps exciton dissociation proceeds in picoseconds

Resources

- Lab
- The WSPC Reference on Organic Electronics, ed J L Bredas, S R Marder (WSPC, 2016)
- Computational Chemistry and Materials Modeling course