

Computational Chemistry and Materials Modeling

## Lecture 5

# Computational Chemistry of Molecules

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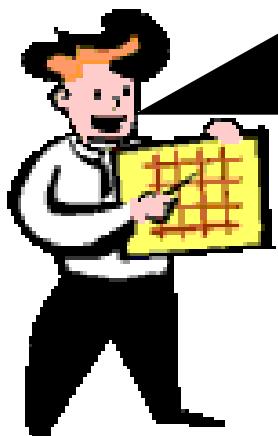
# Outline

- *Practical guide to most common calculations:*
  - Molecular structure
  - Total energies
  - Electronic structure (analysis)
  - Charged and excited states
  - Linear response
  - Batch calculations and benchmarking
  - Complex calculations

# Practical synopsis I



You need to calculate  
electronic structure of  
XXX molecule and  
compare it to experiment



*CC is the  
most accurate  
method in the  
world!!!*

*Use DFT: it is  
mighty and  
practical!*



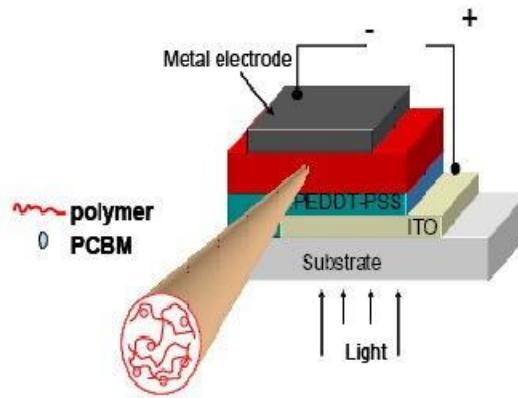
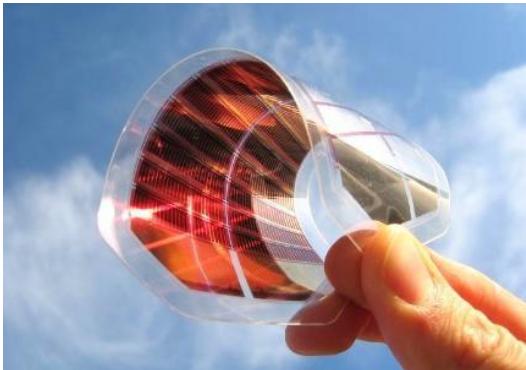
# Practical synopsis II

- There is a multitude of methods and codes, and the obvious choice does not always exist
- There is a law of “conservation of difficulty”, and there is a trade-off between efficiency and transferability
- Use physical sense and chemical intuition to maximize (result)/(spent time), i.e. performance/price ratio

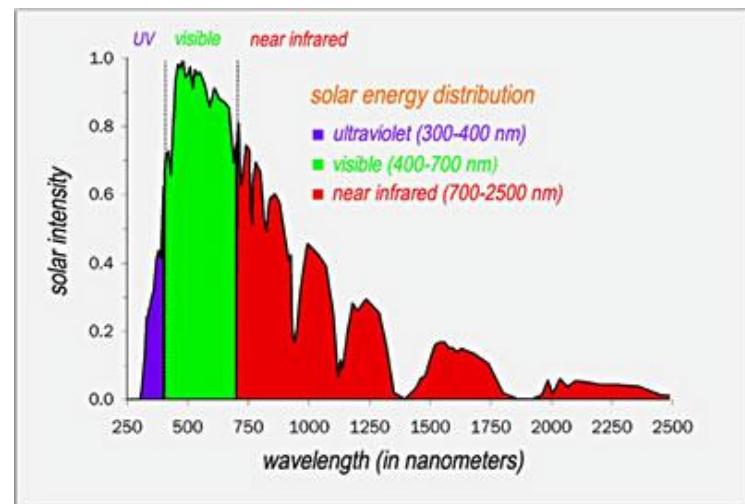
## Philosophy of large molecule calculations

- High accuracy approaches are not feasible
- Benchmarks on small molecules are not usually applicable
- Direct and indirect comparisons with experiment are necessary
- Get the fundamental physics first
- Look to the numbers

# Example: Organic solar cells



- Light creates an exciton
- Exciton produces charges

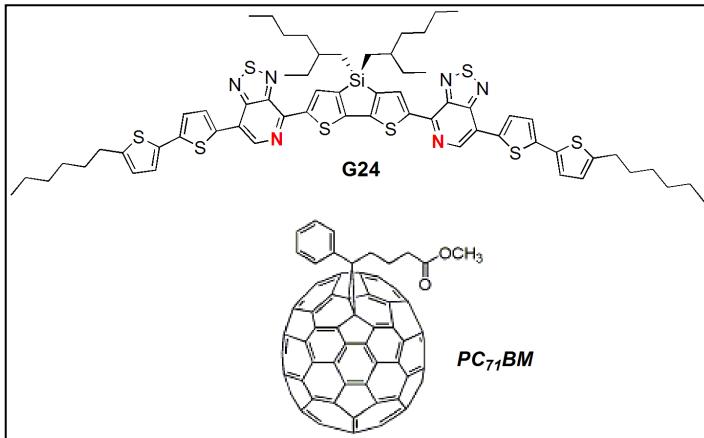


*Usually you will not be asked to calculate something, instead, the problem may be formulated like this:*

*Need new photoactive materials for bulk-heterojunction solar cells (broad absorption spectrum matching the spectrum of solar light + large exciton diffusion length + efficient charge separation at the heterojunction + high hole mobility + ...)*

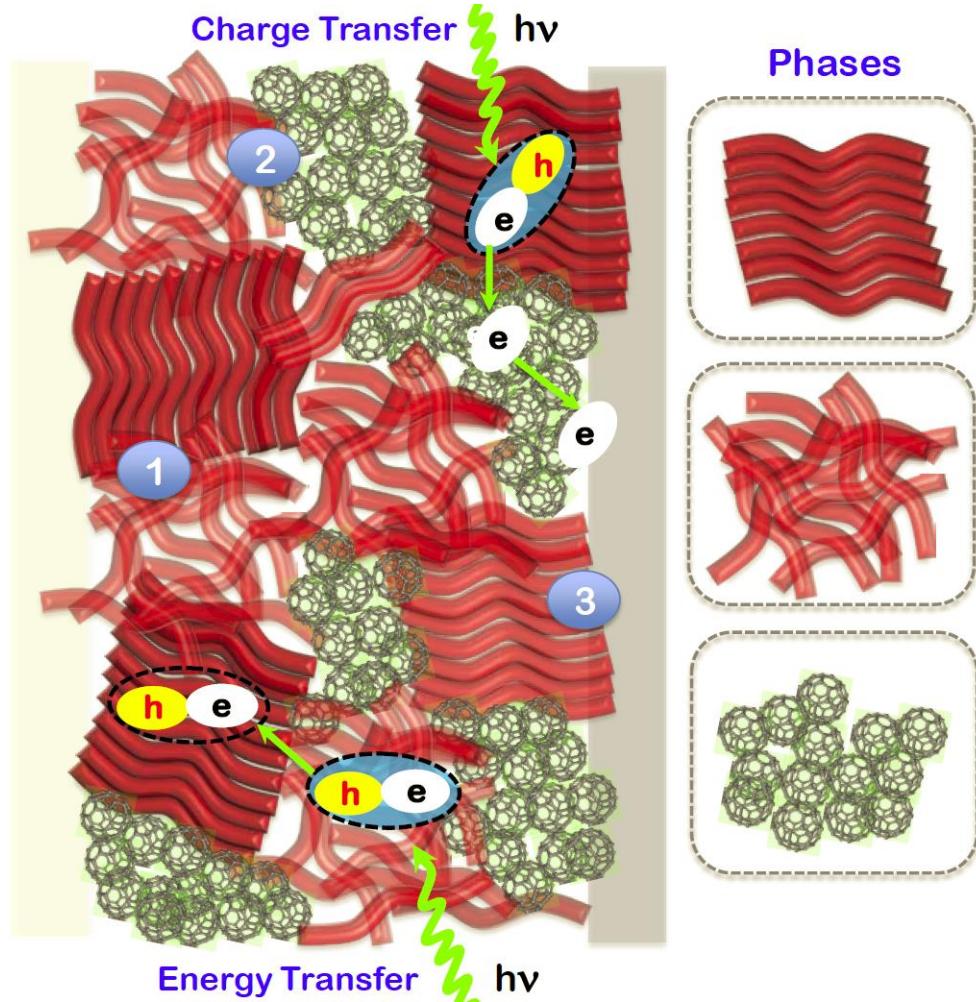
# Example: Organic solar cells

Usually a mix of 2 components: electron and hole conductors



Fundamental processes in 'soft' organic materials: light collection, energy transfer, charge separation, charge transport:

- Conversion of excitation energy (exciton) into electrical/chemical energy (charges) and vice versa.
- Exciton and charge transfer processes as a function of molecular conformations and packing at the interface.
- Carrier injection/extraction from organic materials.



# Molecular structure

- How to get initial guess for geometry
- Geometry optimization (PES extremum)
- If there are multiple minima (PES scan)
- Transition state (saddle point)

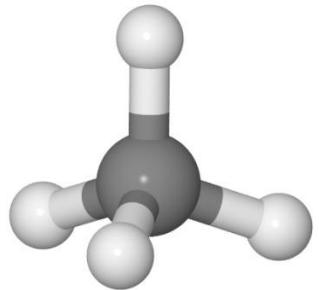
# How to get initial geometry

- Databases: NIST, COD, CCDC, Materials Project  
(clean up, remove disorder, add H)
- Generate from asymmetric unit
- Use internal coordinates (Z-matrix)
- Use molecular/crystal builders
- Enumerate atoms wisely and consistently
- Orient and symmetrize if appropriate
- Store geometries as separate documented files in commonly recognized formats (XYZ or CIF)

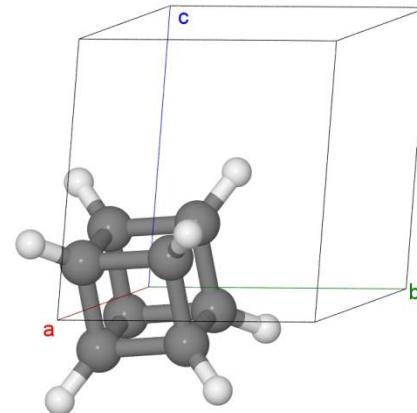
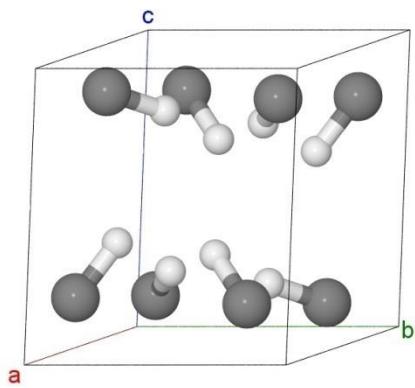
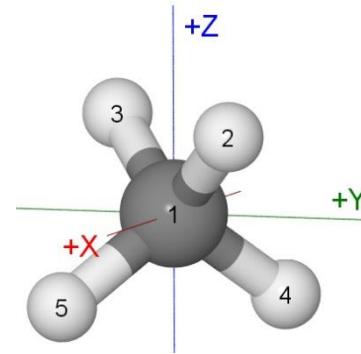
*Wrong initial geometry will nullify all calculations*

# Examples of bad initial geometries

Bad

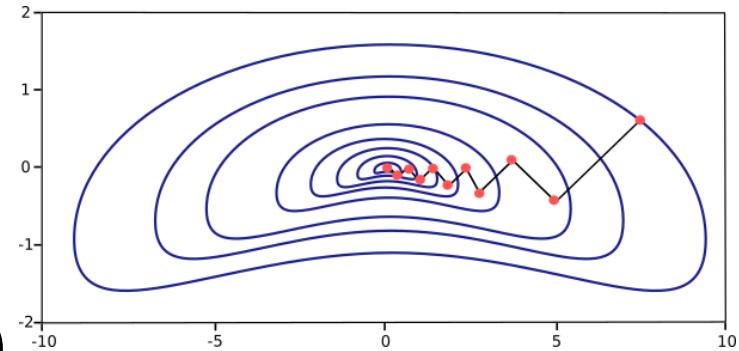


Good



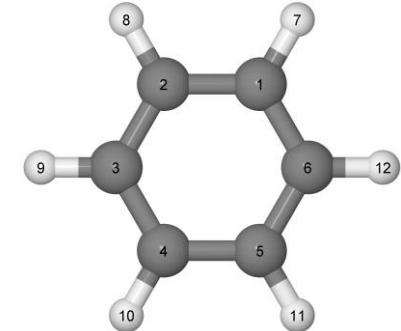
# Geometry optimization: theory

- Usually you will find local extremum on PES  
(Hessian-based methods can find minimum)
- Apply appropriate method:
  - steepest decent
  - conjugated gradients
  - quasi-Newton methods
  - least squares extrapolation methods (DIIS)
  - damped dynamics
- Use analytic gradients and Hessians
- Constrained optimization
  - (by symmetry, by fixing some coordinates)
- Unit cell optimization is a separate problem



# Geometry optimization: practice

- Save geometry after optimization (XYZ/CIF file)
- Do single point to get final energy and gradient
- Check Hessian if feasible
- Is there a symmetry breaking?
- Symmetrize if not done by optimizer
- Use reasonably tough stopping criteria  
(e.g. intermolecular or for Hessian)
- If optimization fails (bad convergence or result):
  - determine the origin of the problem
  - for wave-function convergence see next slide
  - check initial geometry, modify if needed
  - use other algorithm or other coordinates
  - select “best” geometry (min E, min G)

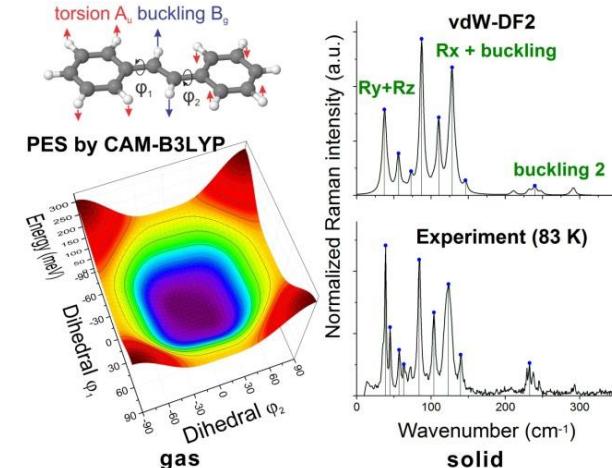
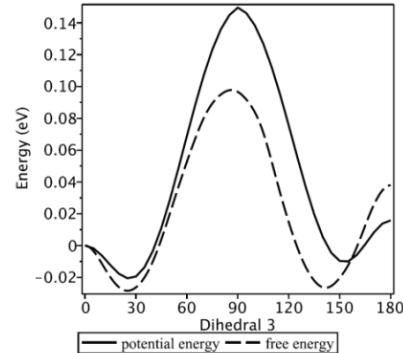
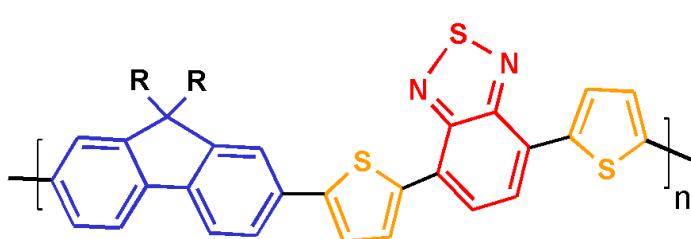


# SCF convergence problems

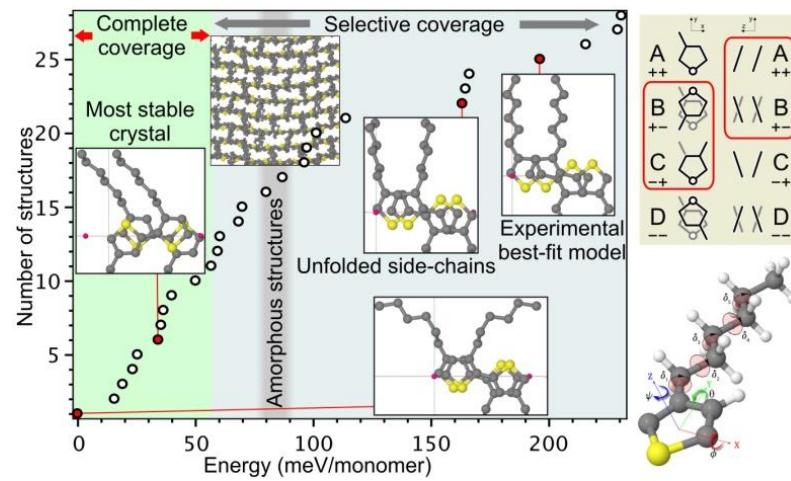
- Determine the origin of the problem
  - Check initial guess for MOs, modify if needed
  - Use other algorithm or tune parameters
  - If gap is small use proper Fermi level smearing
  - Preconverge by other method
  - Converge from other geometry
- 
- Do not weaken convergence stopping criteria!
  - In contrast to geometry optimization, it is often impossible to converge wave-function by a given method in a given program without re-coding

# If there are multiple minima

- Small distortion – use high symmetry structure
- Noncritical side-chains – consider backbone

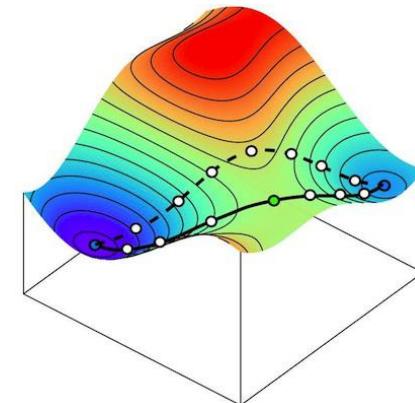


- Few coordinates – scan PES
- Several coordinates – enumerate
- Huge number of conformers:
  - use proper thermodynamic energy
  - use MD or MC to sample
  - use special software, e.g. USPEX code



# Transition state

- Use ordinary optimizer if close to transition
- Use path optimizer if single path:
  - Nudged Elastic Band
  - Quadratic Synchronous Transit
- Use special methods if complex PES



- Be careful if the band gap is small at the transition (electron transfer, chemical reactions, ethylene)

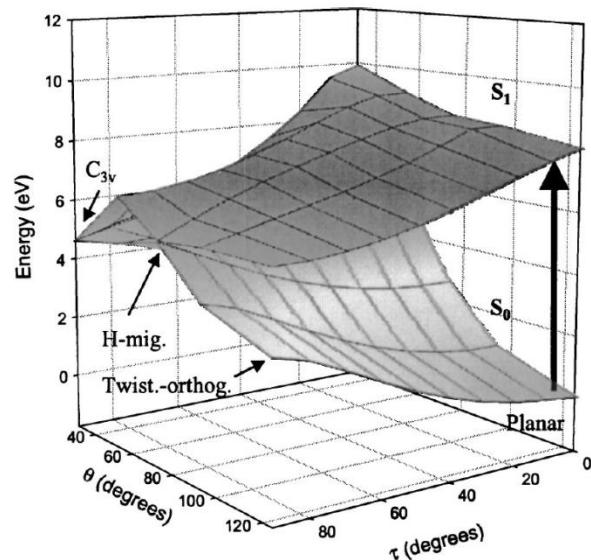
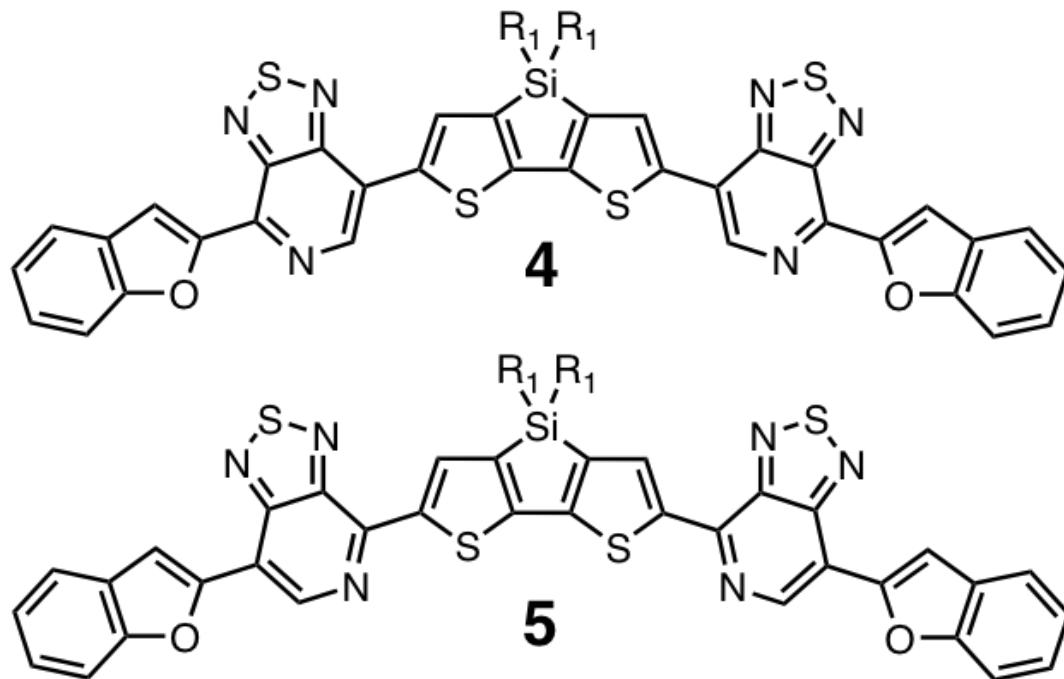


FIG. 9.  $S_0$  and  $S_1$  potential energy surfaces in dependence of the H migration ( $\theta$ ) and the torsion ( $\tau$ ) angles optimized for  $S_1$  state. Calculations performed at the same level as given in Fig. 5. The planar ground-state ethylene energy is the energy zero. DOI: 10.1063/1.1807378

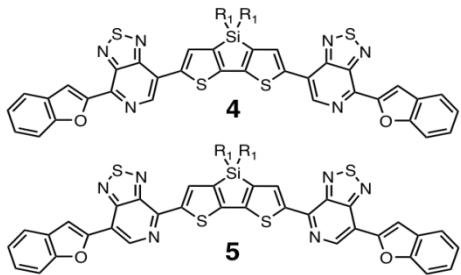
# Example: Barriers and conformers

*Experimentalist: I have synthesized a few new molecules, one seems to crystallize well and the second is not. What is going on?*

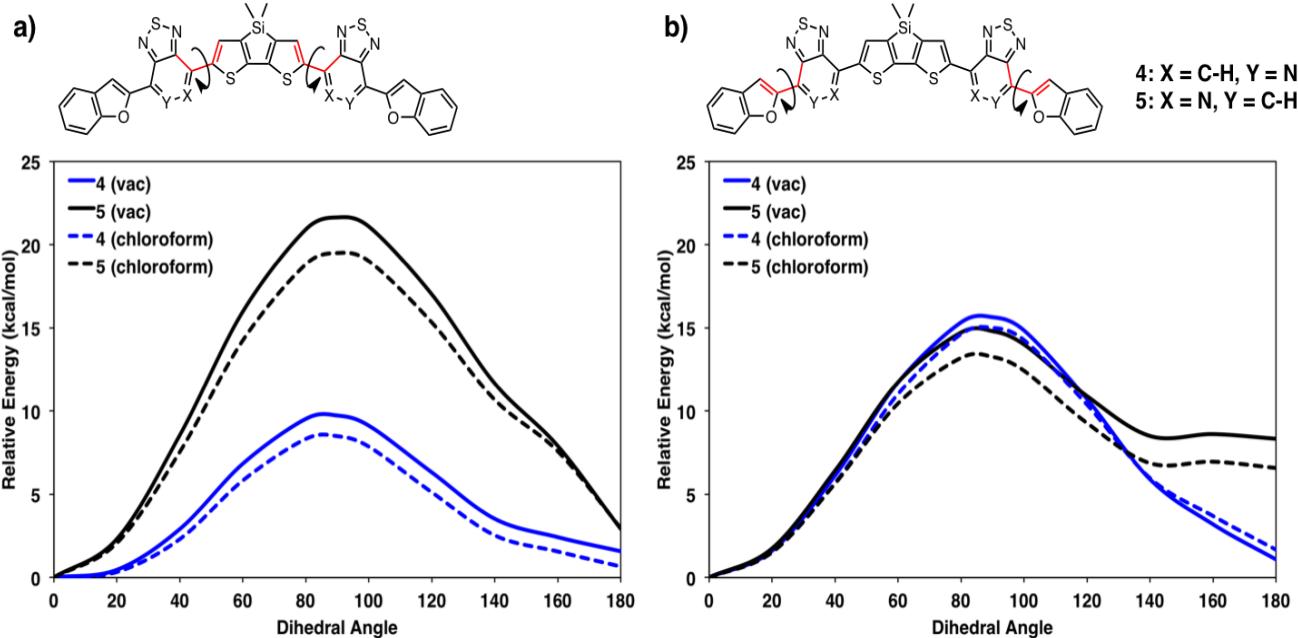


Master Student, how do you approach?

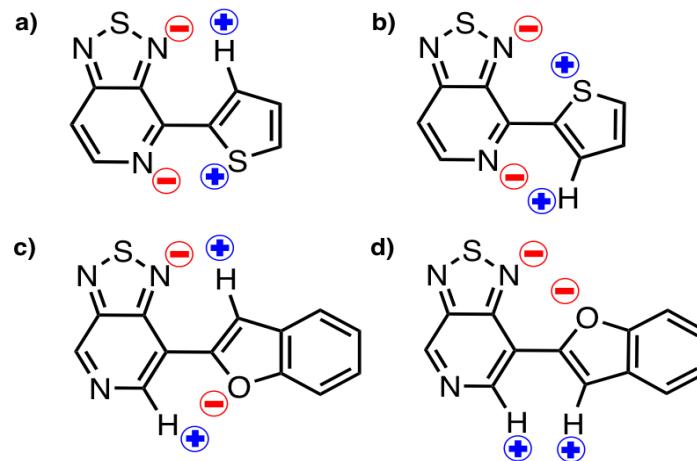
# Example: Barriers and conformers



*Very different energies for rotamers for compound 4, but similar for compound 5.  
Possibly will affect crystallization (multiple conformers in solution will not assemble well!)*



Why? Combination of steric and electrostatic interactions.



# Discussion

1. What if after geometry optimization (a) there are several imaginary vibrational frequencies; (b) several frequencies are close to 0?
2. How do you check if your geometry corresponds to a transition state?
3. In DFT calculations with gradient-based optimization, your final geometry had lower symmetry than the initial one. How could the program code break the symmetry?

# Total energy

- Use relative energies, not absolute – idea behind composite methods
- Use the same method for all comparisons
- Zero-point energy and vibrational free energy
- Avoid basis set superposition error, e.g. by counterpoise correction
- Study dependence on method (basis set, density functional)
- Higher level of theory can be used compared to geometry optimization

# Calculation of heat of formation: molecule in gas phase

## Basic thermodynamics

- Thermal energy  $E(S, V) = E_0 + E_{\text{rot+vib}}(T) + E_{\text{translat}}(T, V)$
- Enthalpy  $H(S, p) = F + pV$
- Free energy  $F(T, V) = E - TS = -T \ln Z$
- For ideal gas  $pV = NT$ ,  $E_{\text{translat}} = (3/2)T$ , and

$$\frac{S}{N} = \frac{5}{2} + \ln \left[ \left( \frac{m_{\text{molecule}}}{2\pi\hbar^2} \right)^{3/2} \frac{T^{5/2}}{p} \right] + \ln(\text{spin multiplicity})$$

## Reference state

- Standard conditions:  $T = 298.15$  K,  $p = 1$  atm
- Atomization energy – fully separated atoms
- Heat (enthalpy) of formation – atoms in their ground states<sup>1</sup>

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<sup>1</sup>H – H<sub>2</sub> gas, O – O<sub>2</sub> gas, Br – Br<sub>2</sub> liquid, C – graphite, S – rhombic sulfur

# Calculation of heat of formation: practical aspects

Challenge: get 1 kcal/mol accuracy, while absolute error in total energy calculation is usually  $\gg 1$  kcal/mol

## Approach 1: Atomization

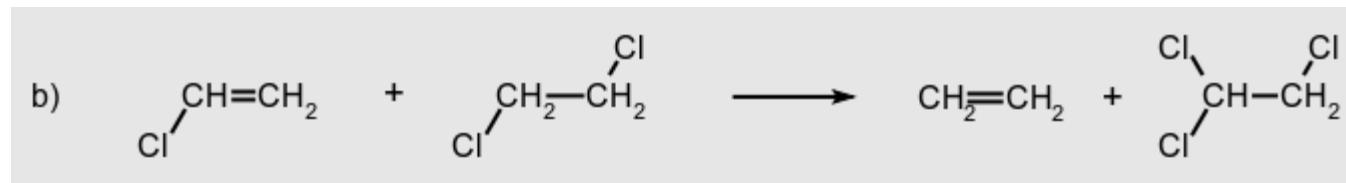
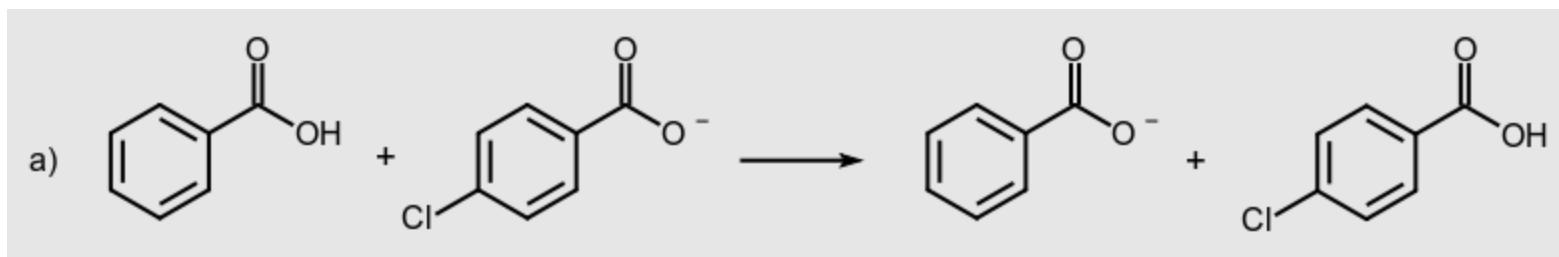
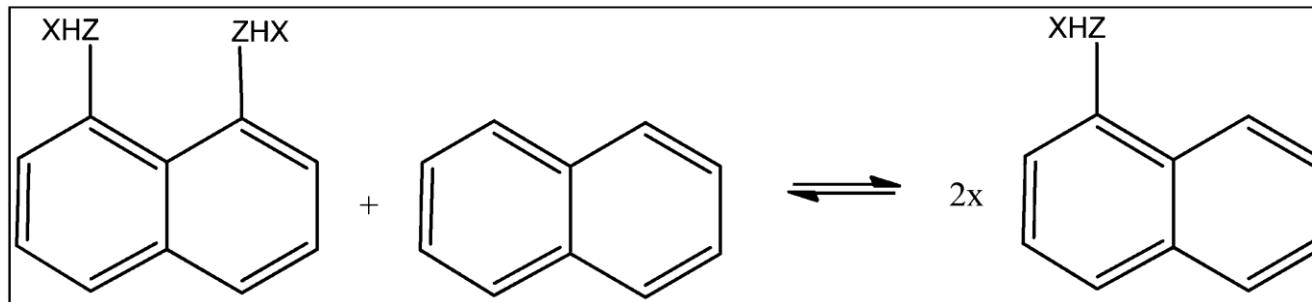
- $X = \sum_i n_i A_i$
- $\Delta H(X) = \sum_i n_i [\Delta H(A_i) - E_0(A_i)] - \frac{5}{2}NT + H(X)$
- Take  $\Delta H(A_i)$  from reference tables
- Calculate  $H(X)$  accurately, e.g. by composite G1-G4 methods
- Use precalculated  $E_0(A_i)$

## Approach 2: Isodesmic reaction

- $X = \sum_i \nu_i Y_i$ ,  $\nu_i$  may be negative and rational
- $\Delta H(X) = \sum_i \nu_i [\Delta H(Y_i) - H(Y_i)] + H(X)$
- Take  $\Delta H(Y_i)$  from reference tables
- Calculate  $H(X)$  and  $H(Y_i)$  with DFT-level accuracy

See also [Accurate Thermochemistry for Large Molecules with Modern Density Functionals](#)

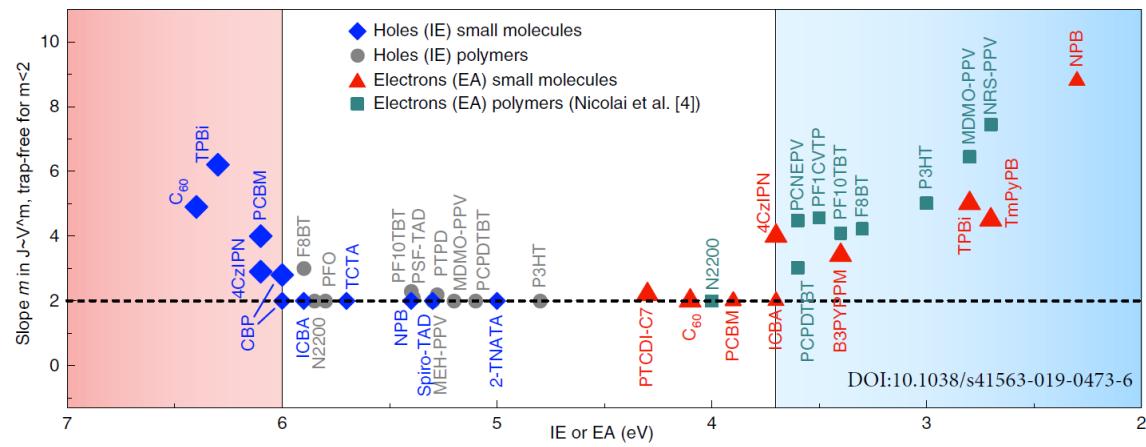
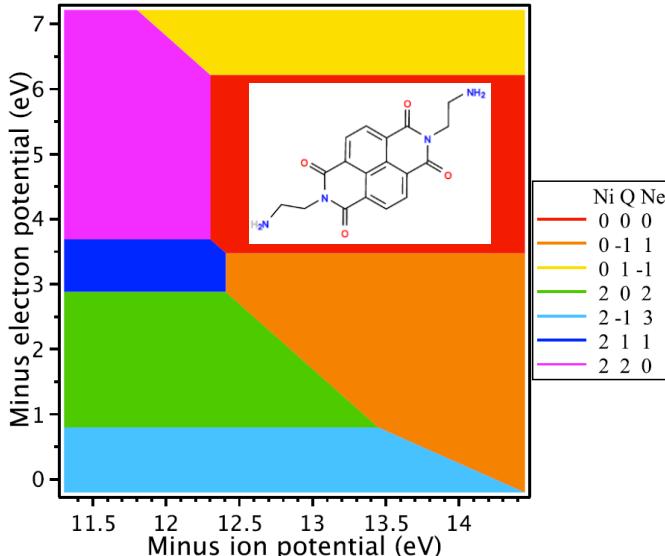
# Example: isodesmic reactions



See also [Error-cancelling balanced reactions](#)

# Varying number of atoms and electrons

- To compare energies use chemical potential ( $\mu$ ):  
 $\mu(X) + E(A) = E(XA)$
- Be careful comparing  $\mu$  in different methods
- What reference value of  $\mu$  can we use:
  - Relevant to problem, e.g. experimental or lowest in your dataset
  - From Standard Hydrogen Electrode (SHE):  
 $2p(aq) + 2e = H_2(g)$ ,  $\mu(e) = -4.44 \text{ eV}$ ,  $\mu(p) \approx -11.37 \text{ eV}$  [DOI:10.1063/1.5000799]  
 this  $\mu(e)$  fits bandgap of semiconductors,  $\mu(p)$  depends on pH



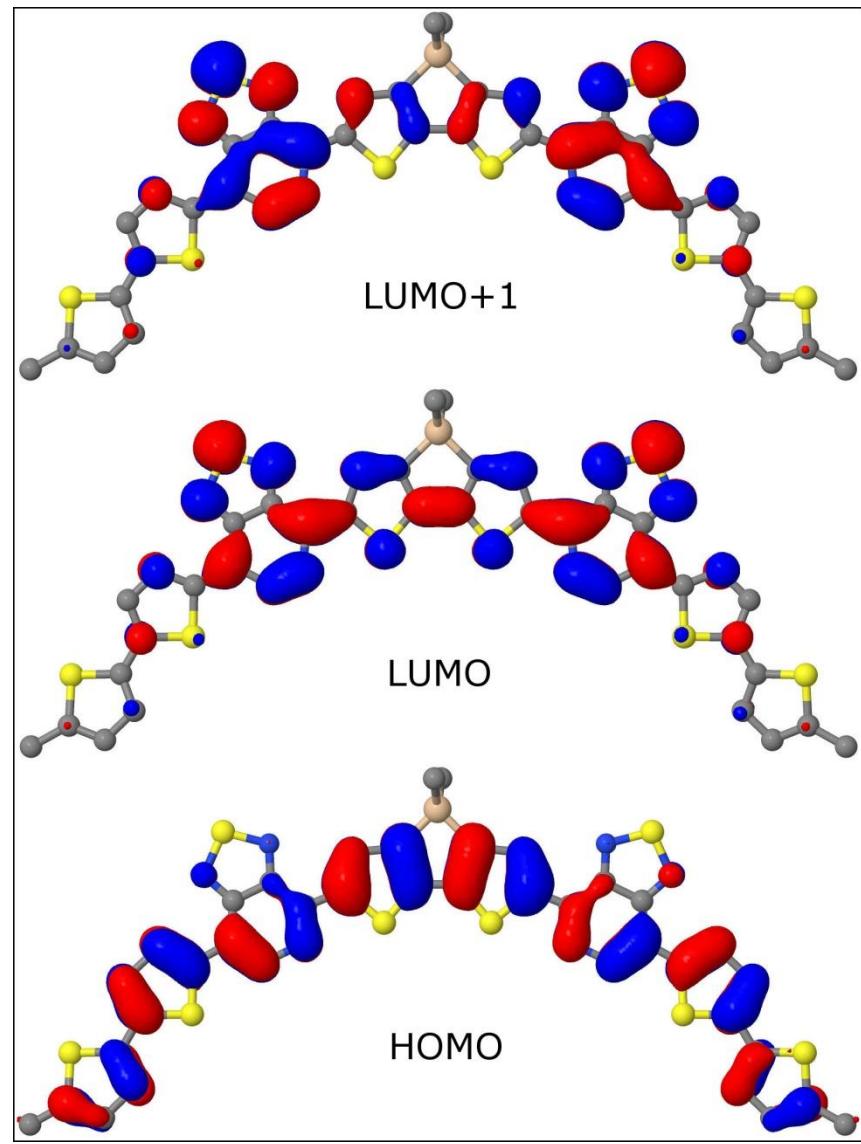
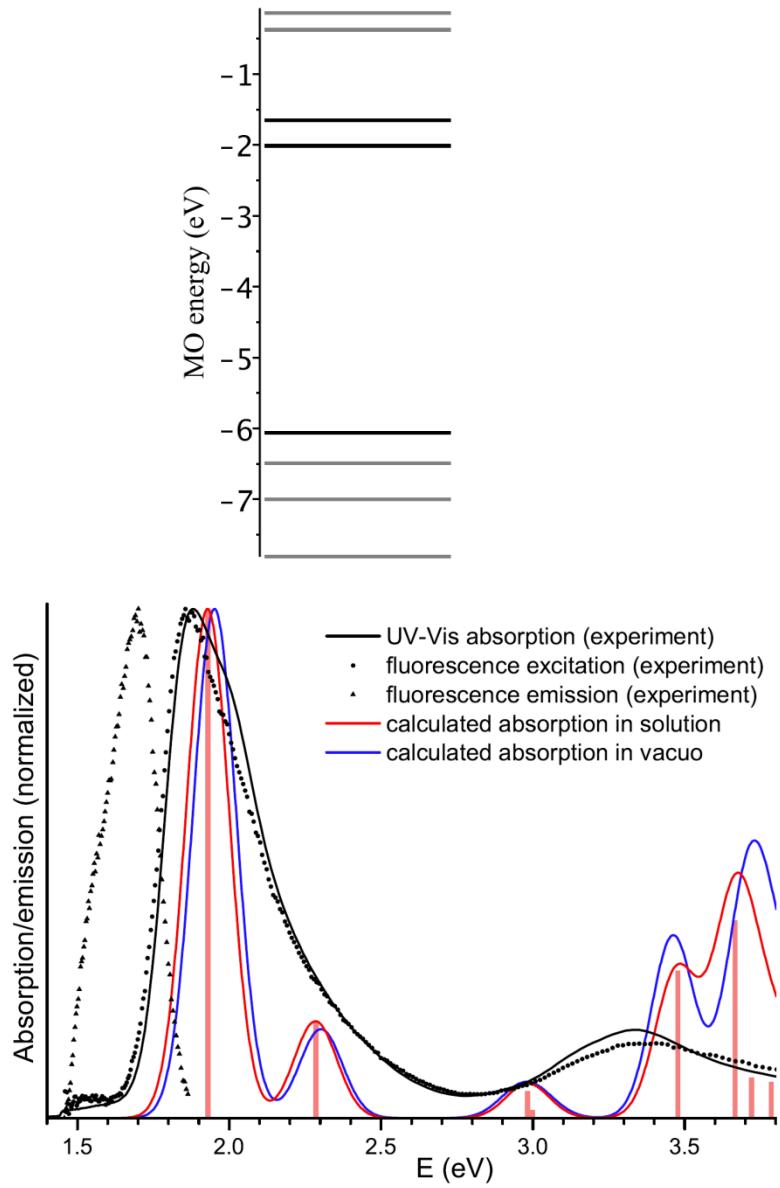
# Discussion

1. You need to calculate alkali ion intercalation potential in a  $\pi$ -conjugated organic material. What is the challenge and how to overcome it?
2. You are calculating a shallow dihedral PES by [DF-LCCSD\(T\)-F12](#) and get a very strange looking curve. What is wrong?

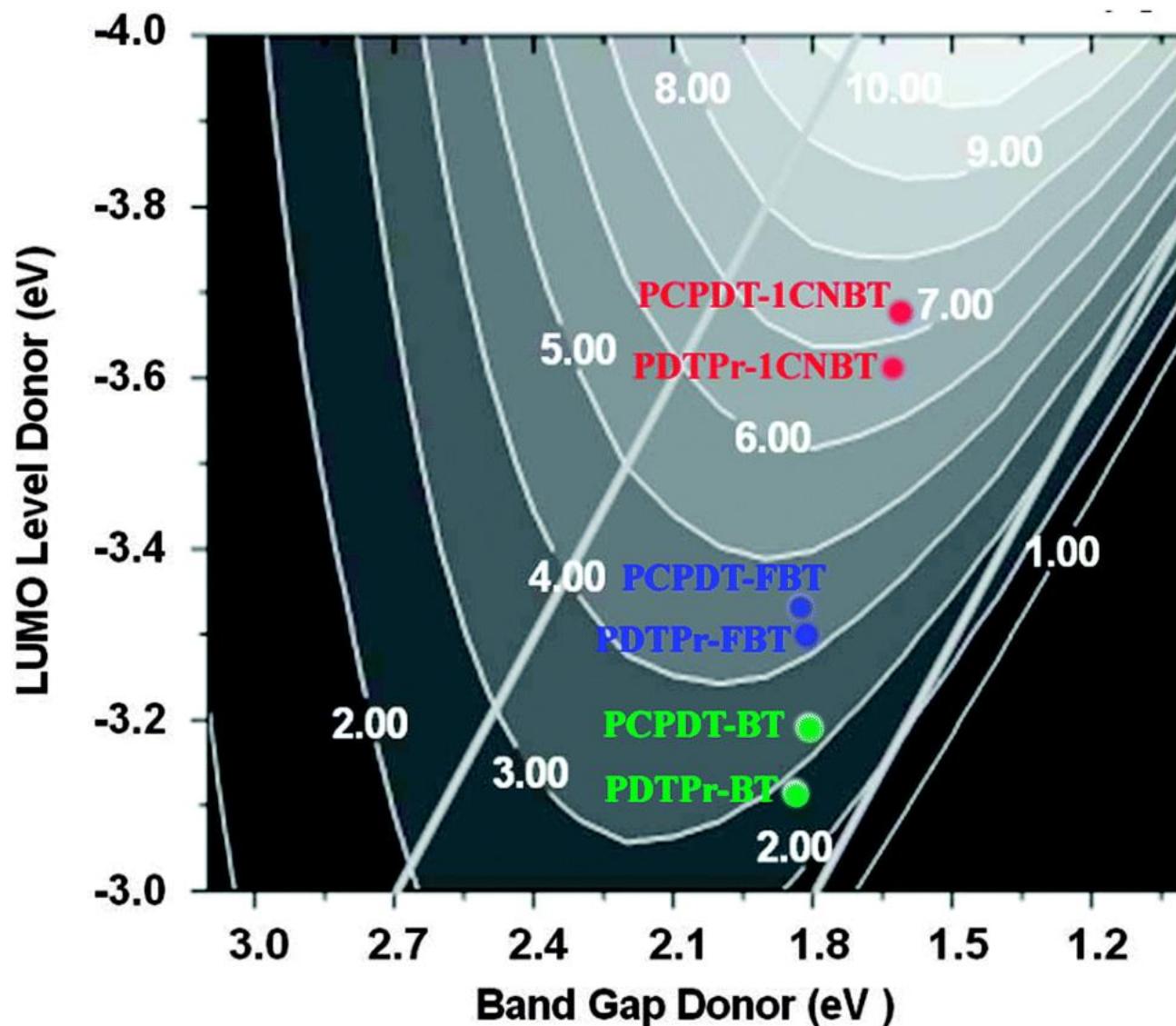
# Electronic structure (analysis)

- We are talking about 1e properties
- Analysis of 1e Hamiltonian:
  - molecular orbitals (MO), frontier MO, LMO
  - DOS, band structure  $E(k)$
- Analysis of 1e density matrix and 1e density:
  - population analysis, atomic charges and bond orders
  - natural orbitals and natural transition orbitals
  - natural bond orbital (NBO) analysis
- 1e density -> electrostatic field (multipoles)

# Example: organic solar cells

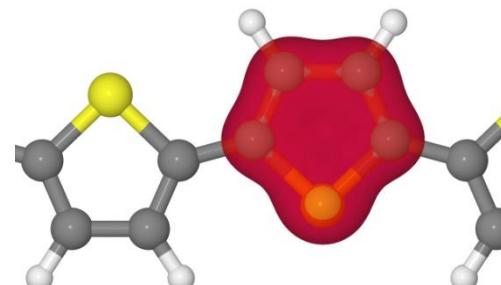
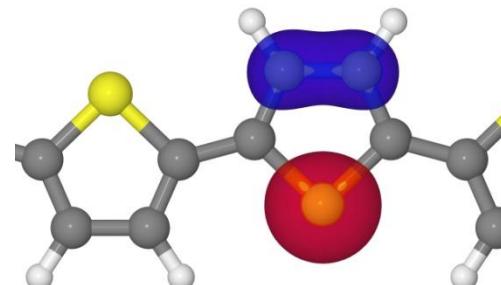
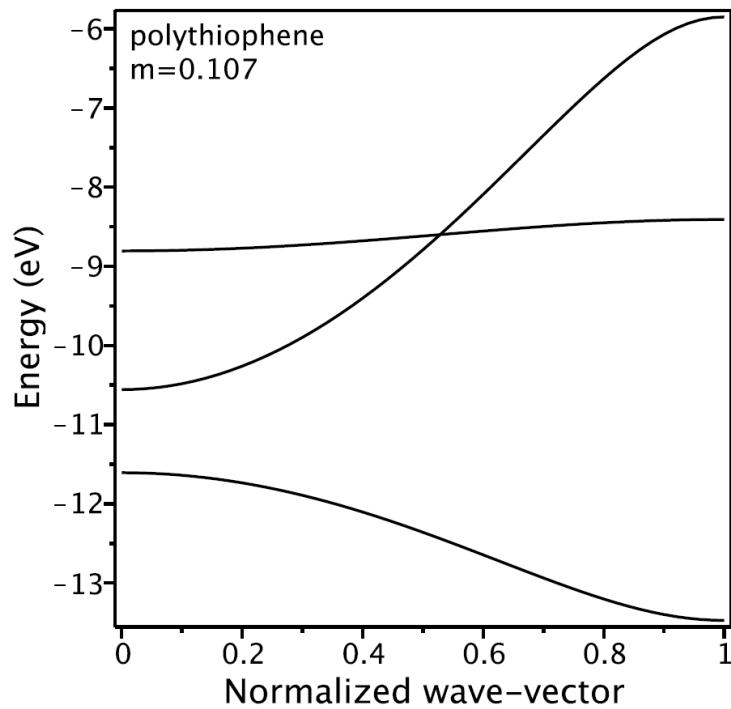
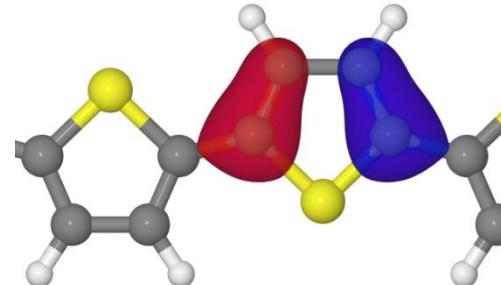
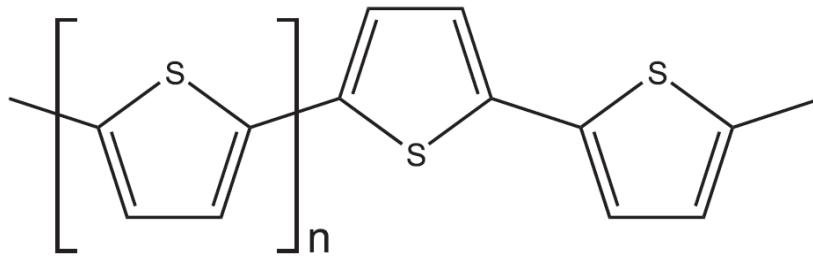


# ... organic solar cells: Scharber's plot



# Example: LMO in polymers

If unit cell has >20 atoms band structure is not informative



# 1e orbitals: definitions

- molecular orbitals (MO) – eigenfunctions of one-electron Hamiltonian (HF/DFT)
- localized molecular orbitals (LMO) – a rotation of MOs localizing each orbital in space
- natural orbitals (NO) – eigenfunctions of one-electron density matrix  $\rho_{\Psi}^{1e}(\xi; \eta) = N \int \Psi(\xi, \zeta_2, \dots, \zeta_N) \overline{\Psi}(\eta, \zeta_2, \dots, \zeta_N) d\zeta$
- natural transition orbitals (NTO) – the same for transition density matrix  $\rho_{\Psi\Phi}^{1e}(\xi; \eta) = N \int \Psi(\xi, \zeta_2, \dots, \zeta_N) \overline{\Phi}(\eta, \zeta_2, \dots, \zeta_N) d\zeta$

# MO vs NO

	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 $n_h = 1 + .17$ $n_e = 1 - .18$		

# NO vs NTO

	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 $n_{h/e} = 1 \pm .25$		

# Atomic charges and bond orders

*It is the simplest yet usually sufficient analysis of 1e density matrix*

## Basic approach – Mulliken charges and bond orders:

- Atomic charge

$$\rho_A = \sum_{\alpha \in A}^{M_{\text{basis}}} \sum_{\beta}^{M_{\text{basis}}} D_{\alpha\beta} S_{\alpha\beta} \quad Q_A = Z_A - \rho_A$$

- Bond order between two atoms

$$\text{BO}_{AB} = \sum_{\alpha \in A}^{M_{\text{basis}}} \sum_{\beta \in B}^{M_{\text{basis}}} (\mathbf{DS})_{\alpha\beta} (\mathbf{DS})_{\beta\alpha}$$

- But sensitive to basis set

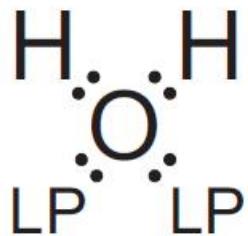
## Advanced – Weinhold's Natural Bond Orbital (NBO) analysis:

- NAO (Natural Atomic Orbitals): orthogonalized orbitals localized on atoms → comprehensive analysis of AO populations (e.g. 3s, 4d<sub>xy</sub>)
- NBO (Natural Bond Orbitals): orthogonalized orbitals localized on bonds (e.g. σ, π\*) or atoms (e.g. LP, core, Ry)

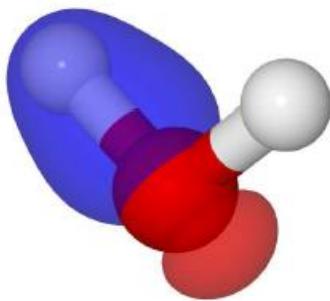
*From NBO website: More precisely, NBOs are an orthonormal set of localized "maximum occupancy" orbitals whose leading N/2 members give the most accurate possible Lewis-like description of the total N-electron density.*

# Example: LMO/NBO analysis of bonding

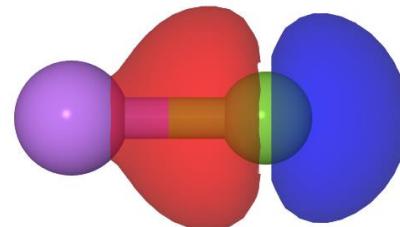
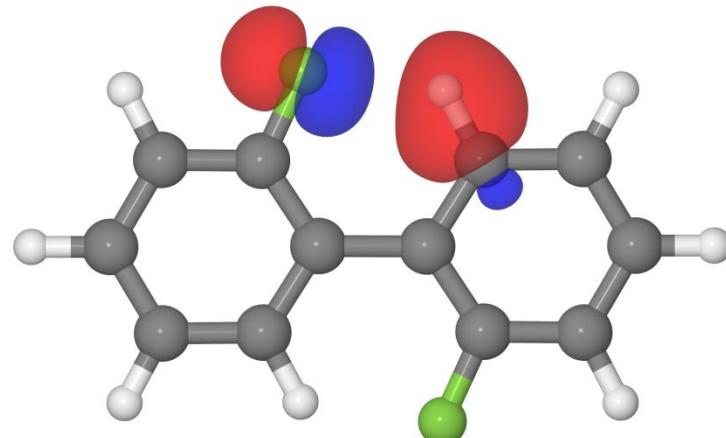
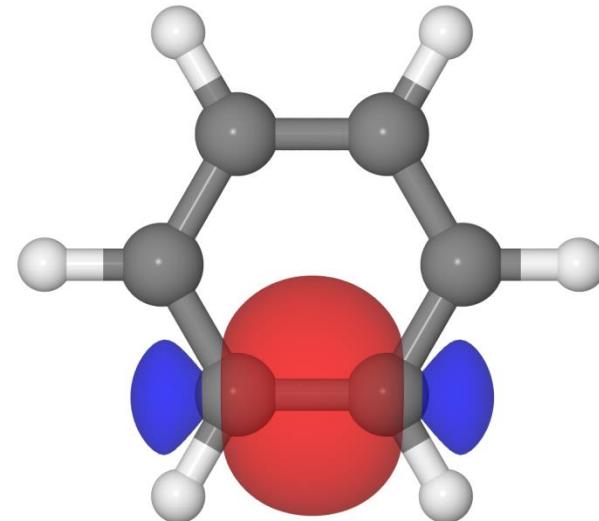
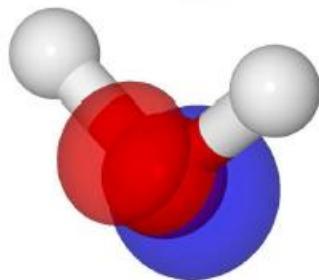
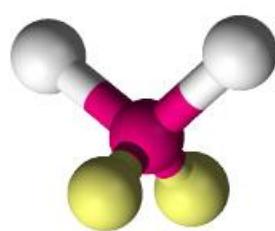
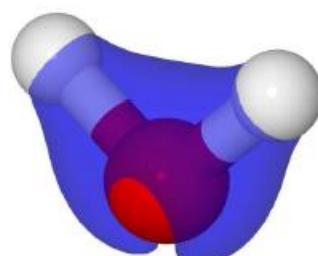
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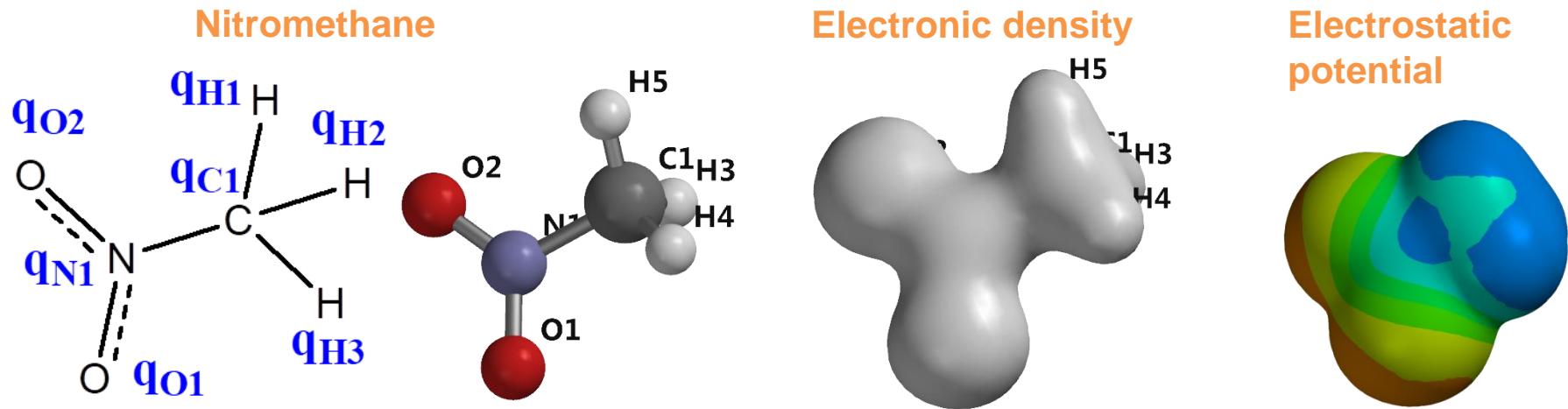
LMO



e-density



# Atomic charges from charge density

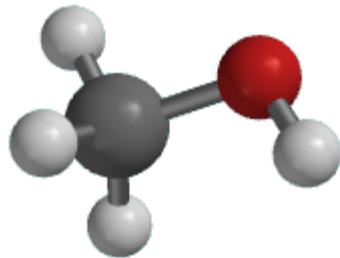
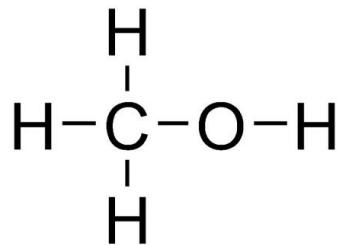


Used for force field parameterization, IR spectra etc

There are different charge partitioning schemes:

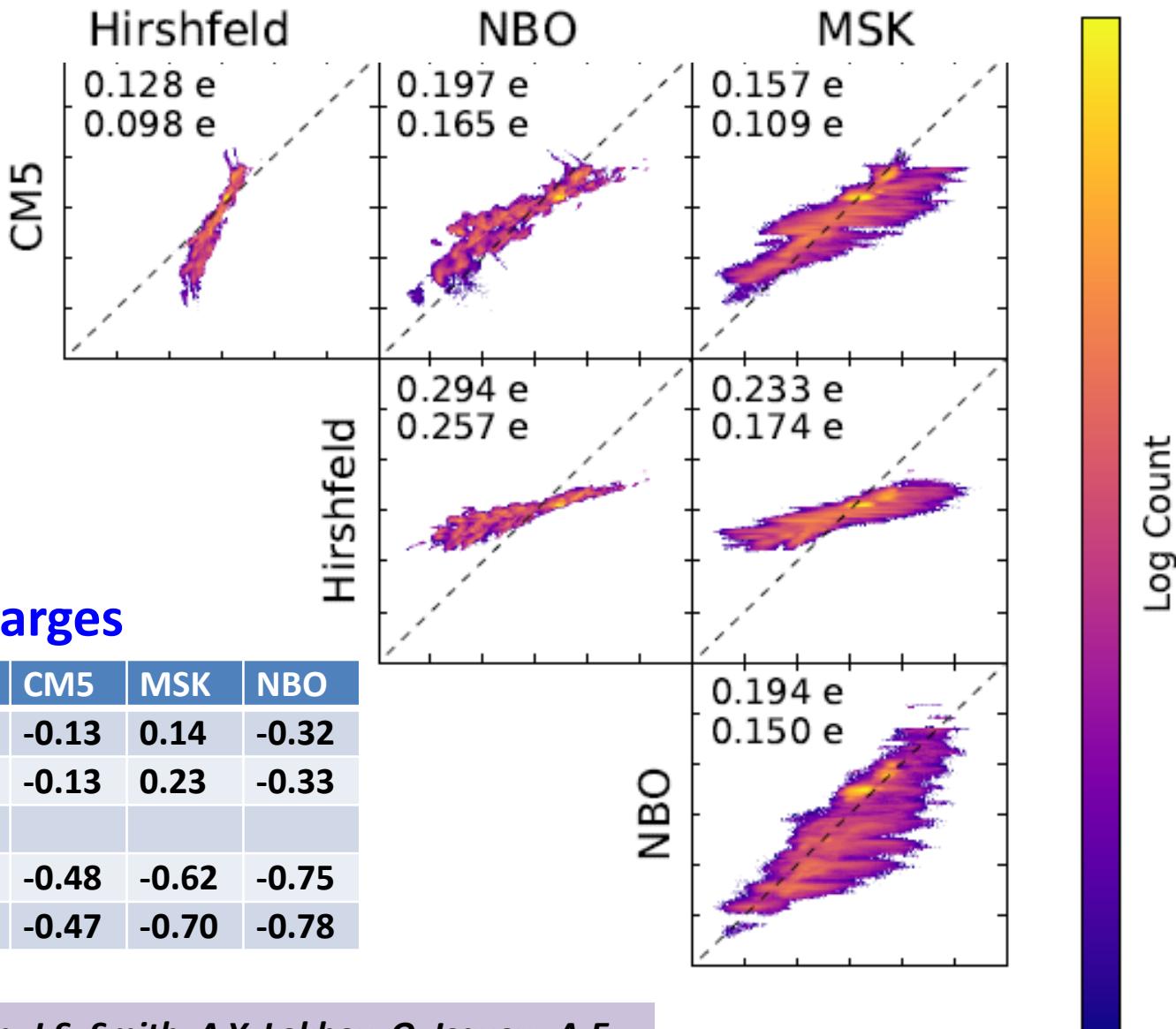
- **Mulliken and NBO:** not designed to represent charge density
- **Hirshfeld:** among first charges (1977) to work well in force fields
- **Charge model 5 (CM5):** improved Hirshfield, better dipoles (2012)
- **Electrostatic potential fitting (ESP):** MSK (1984), CHELPG, charges depend on what region to fit
- **Machine learning:** see next slides [J Phys Chem Lett 9, 4495 (2018)]

# Atomic charge schemes do not agree!



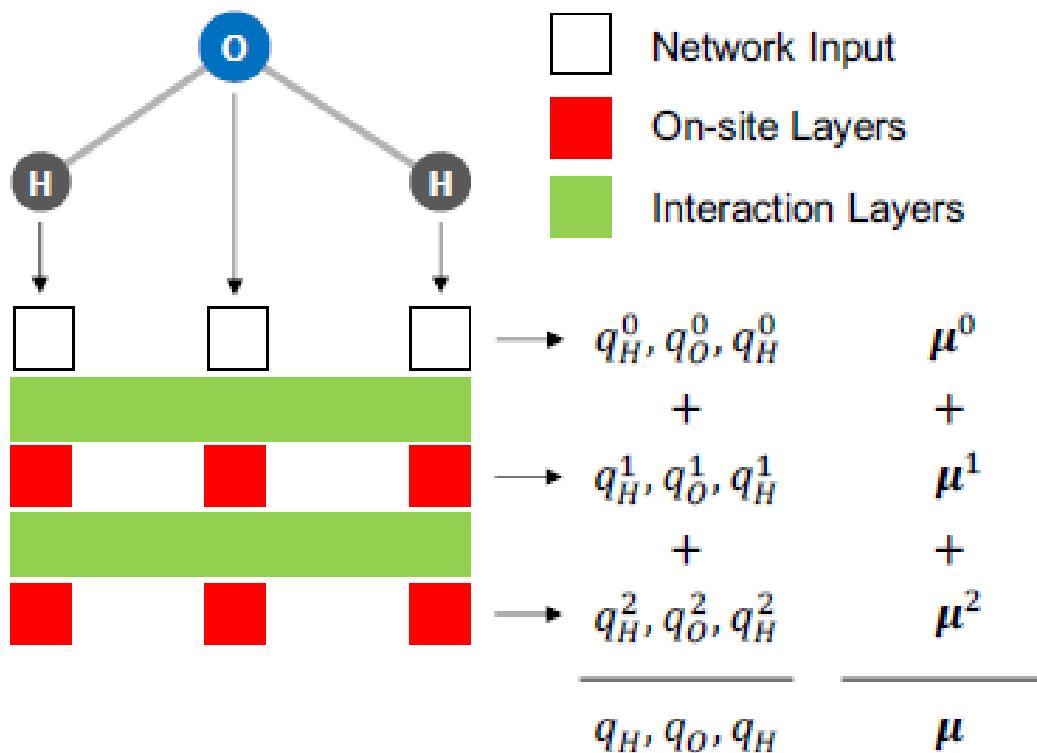
## Methanol charges

Carbon	Mulliken	Hirshfeld	CM5	MSK	NBO
6-31g*	-0.23	-0.007	-0.13	0.14	-0.32
6-31+g*	-0.36	-0.01	-0.13	0.23	-0.33
Oxygen					
6-31g*	-0.62	-0.26	-0.48	-0.62	-0.75
6-31+g*	-0.66	-0.25	-0.47	-0.70	-0.78



# ML Affordable Charge Assignment (ACA)

Can we choose atomic charges such that the point charge calculation of the dipole reproduces the *ab initio* dipole?



Hip-NN neural nets  
ANI-1X training set  
Reference DFT:  
wB97x/6-31g(d)

$$\mu^{ML} = \sum_i^{N_{atoms}} q_i \mathbf{r}_i$$

$$\mu^{REF} = \langle \psi | \rho \mathbf{r} | \psi \rangle$$

Cost function

$$\mathcal{L} = \langle (\mu^{REF} - \mu^{ML})^2 \rangle_{Dataset}$$

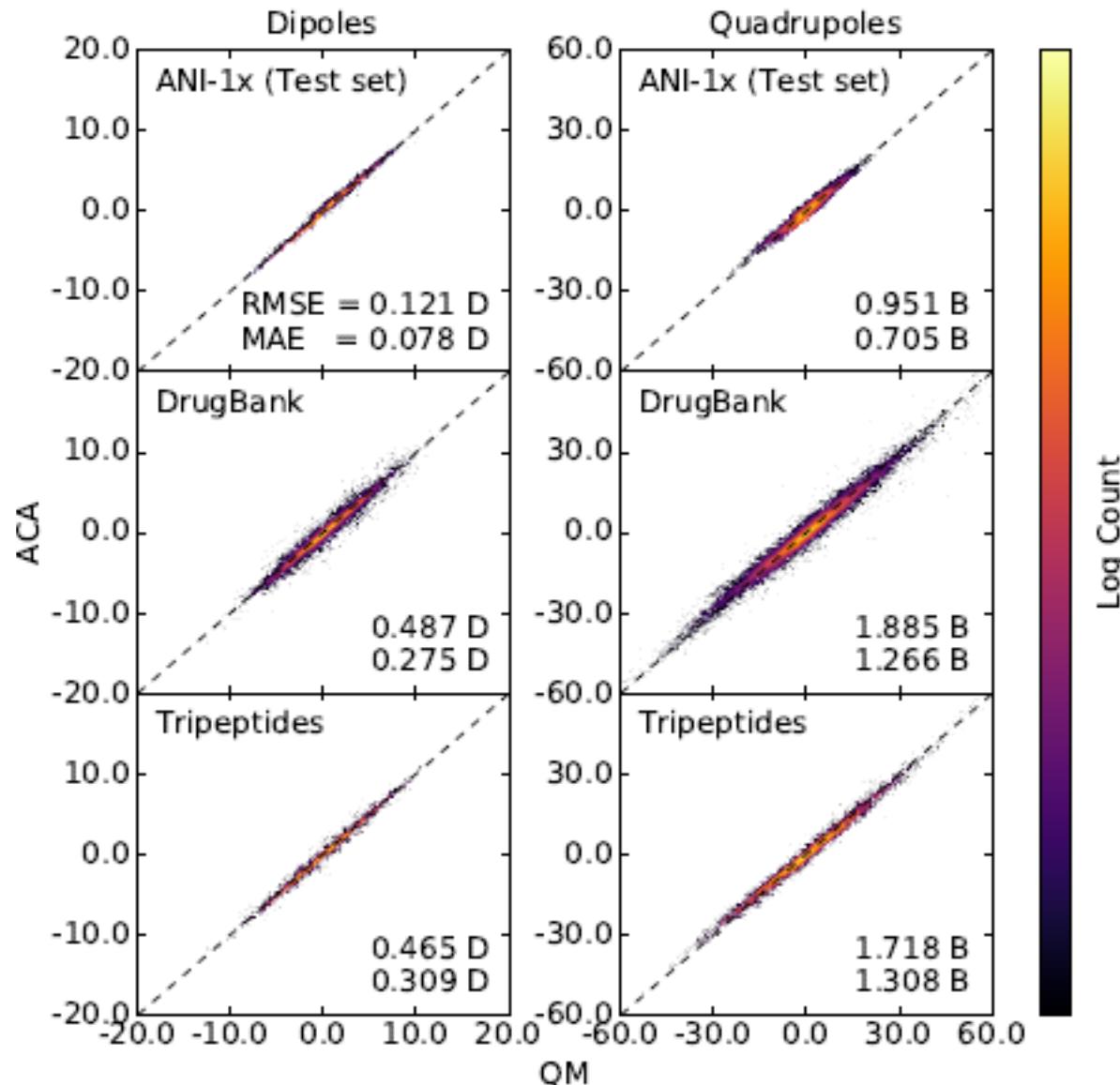
Only ground state dipoles were learned!

# Dipole and quadrupole predictions

Dipole accuracy  
~0.1-0.5 Debye

Quadrupoles are ‘for free’ - never trained.  
The accuracy ~1-2 Barns  
( $C^*m^2$ )

*The accuracy ‘per atom’ is the same across all datasets!*



# Discussion

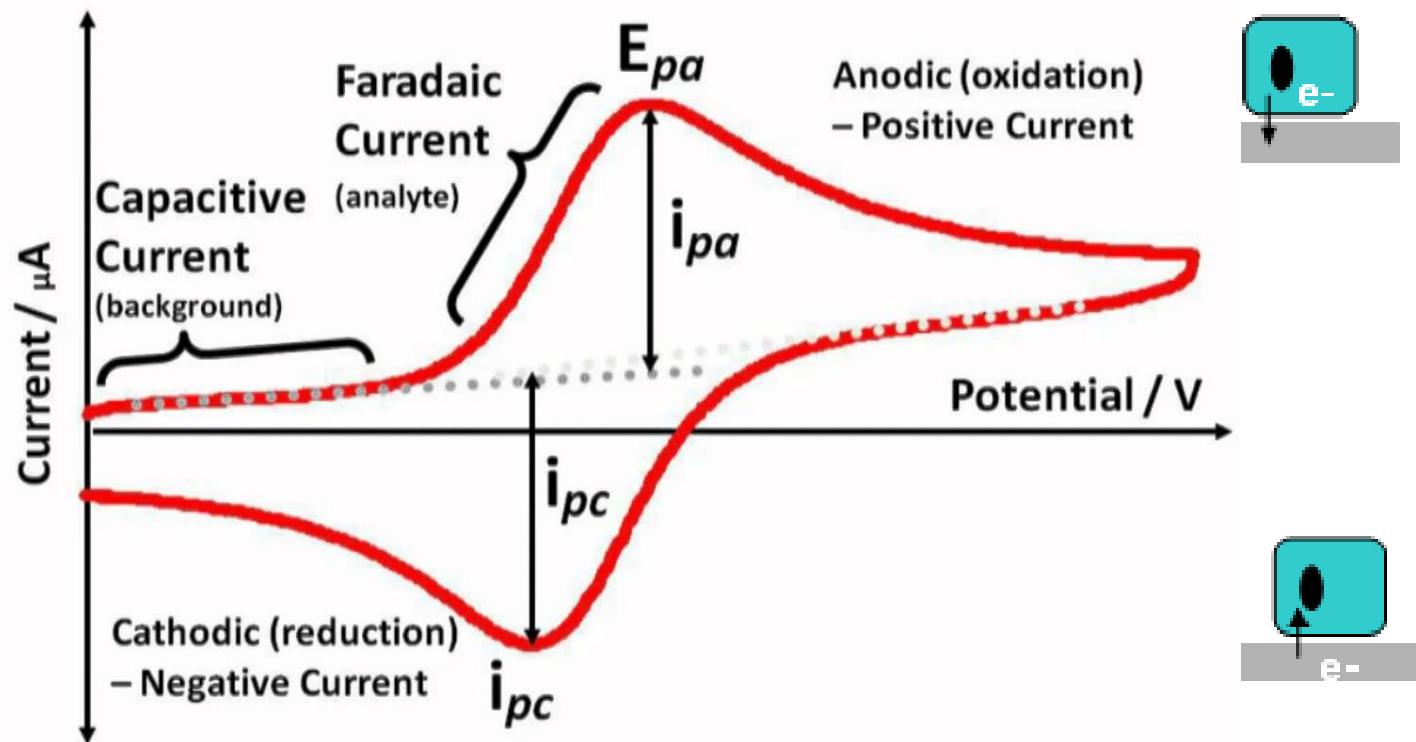
1. Define bonding and antibonding MOs.
2. Why one can take a superposition of MOs, for example, to form LMOs?
3. Explain why for some atoms in large molecules ESP charge fitting might be not a robust approach.

# Charged and excited states

- Cation, anion, singlet exciton, triplet exciton
- Energy gaps, IP/EA, absorption/emission energies
- Vibronic (electron-phonon) couplings
- Jahn-Teller effect

# IP and EA

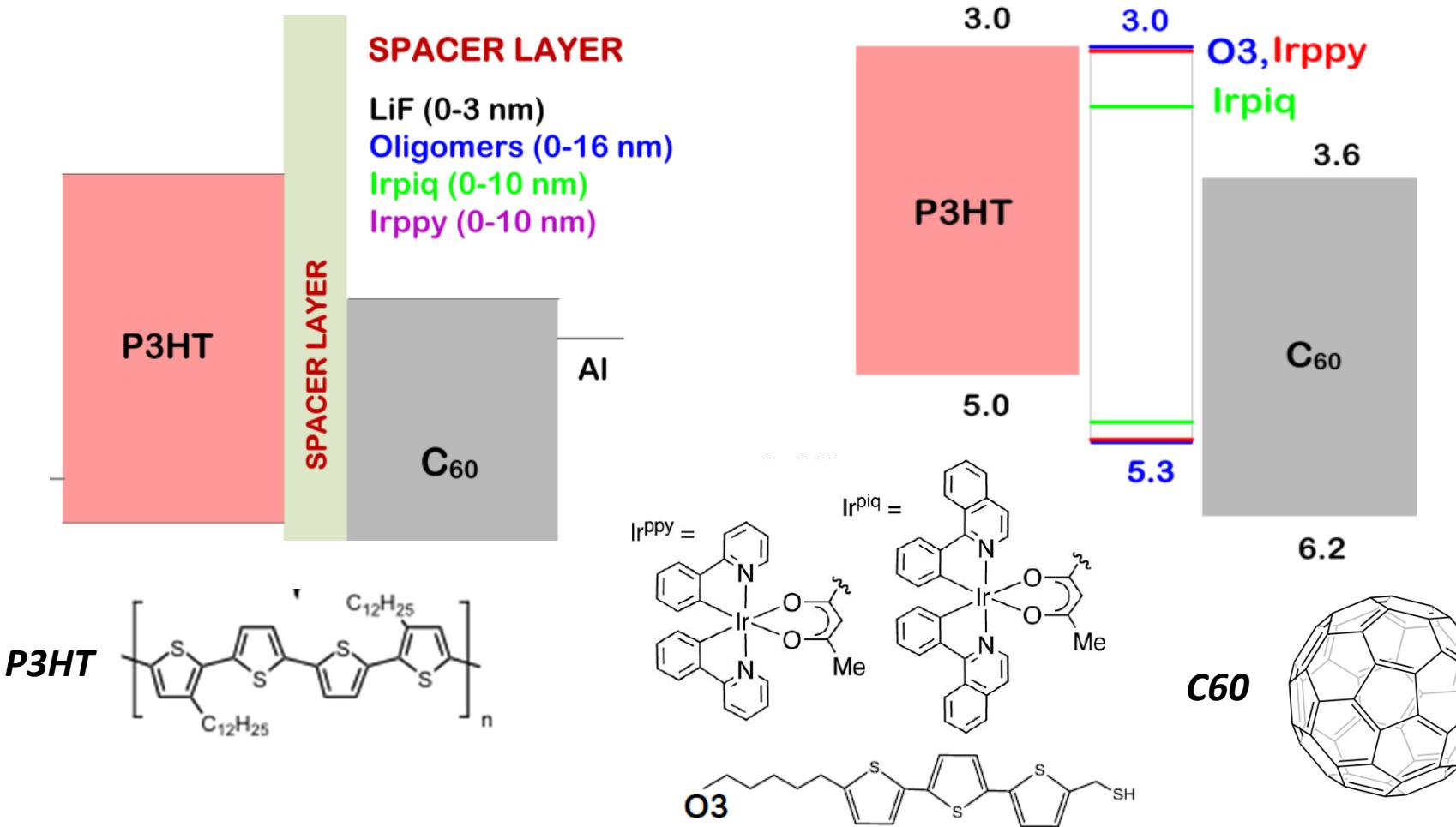
## Cyclic Voltammogram



**Cyclic Voltammetry:** experimental characterization technique using a reversible electron transfer allowing evaluation of Electron Affinity (EA) and Ionization potential (IP) - although quite inaccurate

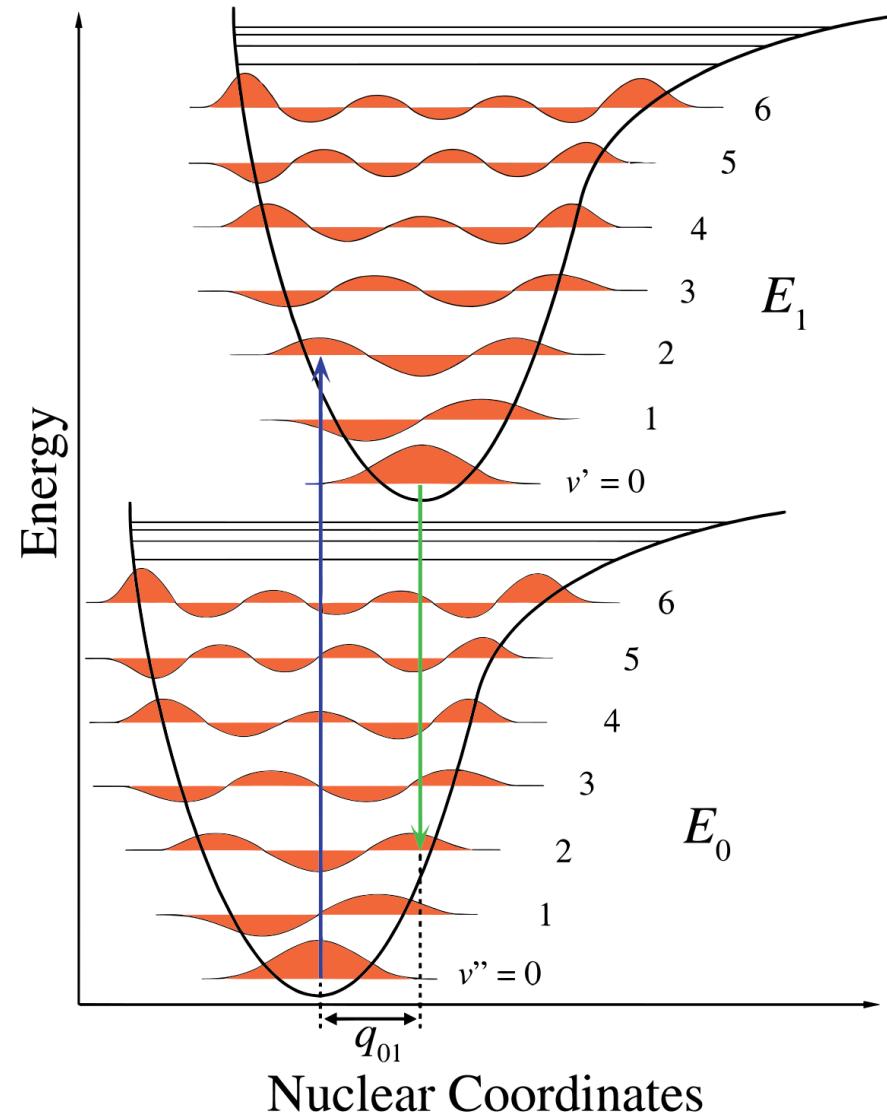
# Example: organic semiconductors

*Experimentalist: I have prepared a prototype device and trying to understand how electron and hole energies are lining up in different materials. Cyclovoltammetry gives me the following numbers. Does it make sense?*



# Vertical and adiabatic IP

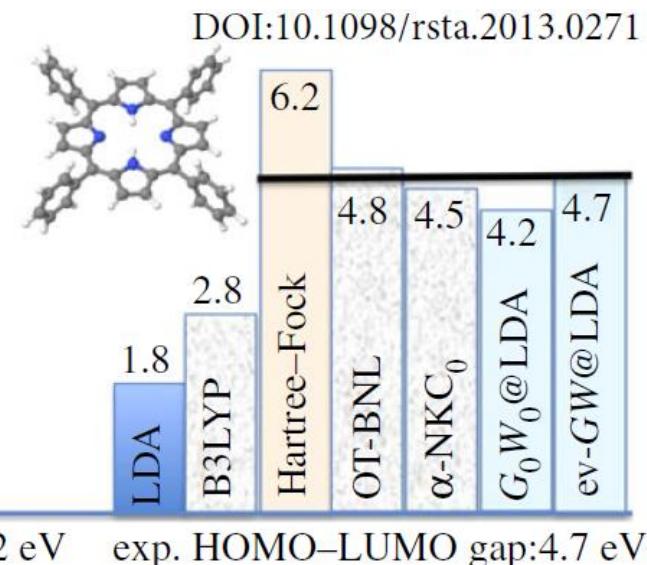
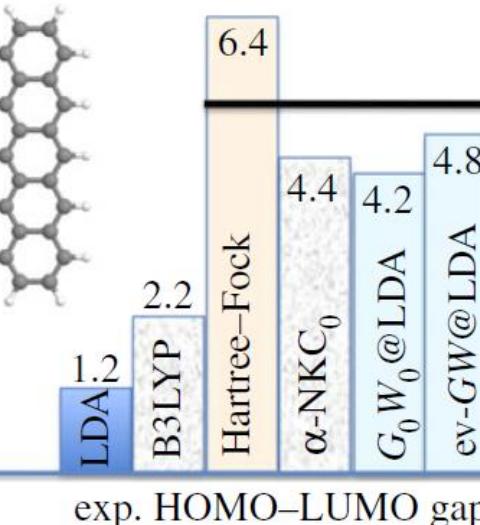
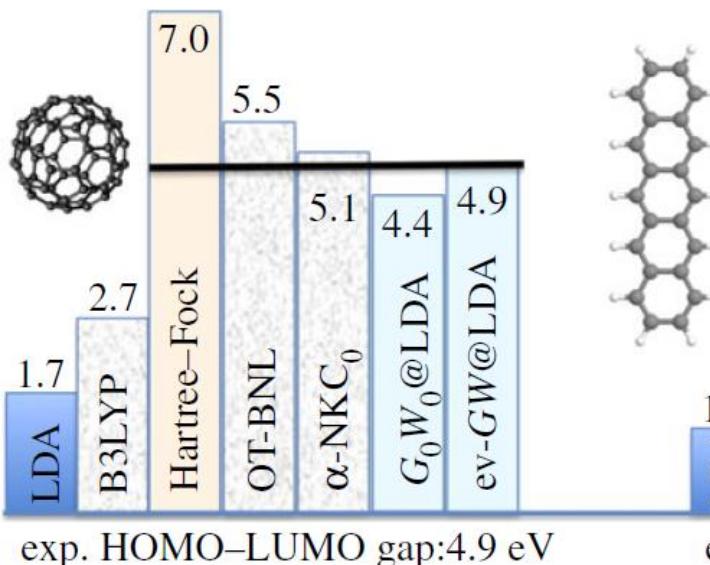
- $\text{IP} = E(Q=+1) - E(Q=0)$
- Koopman's theorem:  
 $\text{IP}_{\text{vert}} = -E(\text{HOMO})$



# IP-tuning of density functionals

Idea: tune density functional (in the example below, range separation parameter) by requiring  $IP+E(HOMO)=0$

$$\frac{1}{r_{12}} = \frac{1}{r_{12}} \left\{ 1 - \left[ \operatorname{erf}(\mu r_{12}) \right] \right\} + \frac{1}{r_{12}} \left[ \operatorname{erf}(\mu r_{12}) \right]$$

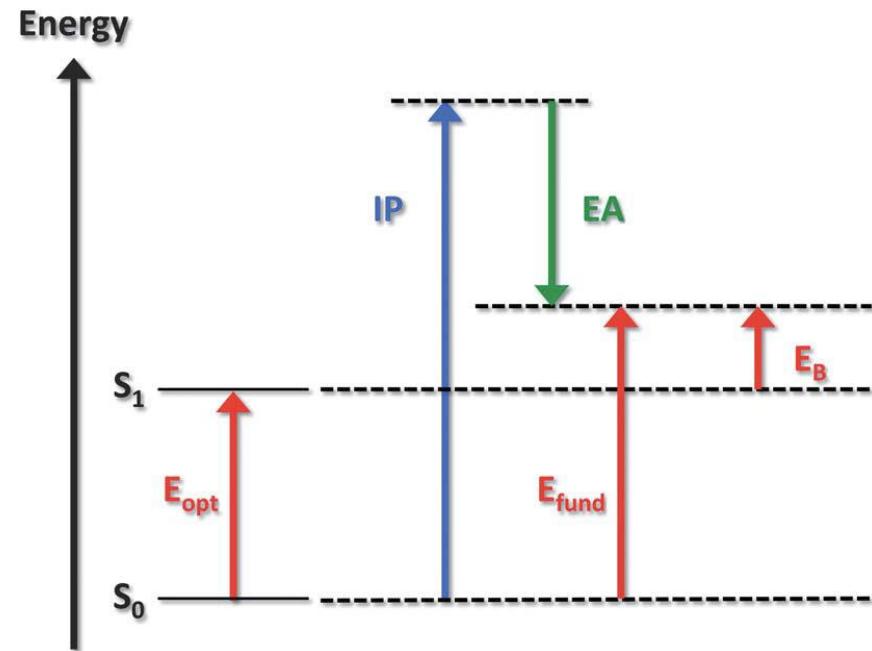


While excellent results were achieved for medium sized molecules, the limiting case to the bulk falls back to the GGA limit due to lack of proper treatment of dielectric effects

# Mind the gap

J Bredas, Mind the gap, Mater Horiz 1, 17 (2014)

- Charge gap (IP-EA)  
(fundamental or transport gap)
- Optical gap ( $S_1-S_0$ )  
(absorption edge)
- Spin gap ( $T_1-S_0$ )
- HOMO-LUMO gap  
(!experimentalists interpret it either as optical or charge gap!)
- Band gap center  $(-\text{IP}-\text{EA})/2$   
(minus Mulliken electronegativity)
- For closed shell systems charge gap > optical gap > spin gap
- For strong correlations one of the gaps approaches zero
- By default all gaps are vertical (only electronic relaxation), but adiabatic gaps (also nuclei relaxation) are also meaningful



# Vibronic couplings

Used in spectroscopy and charge transport studies

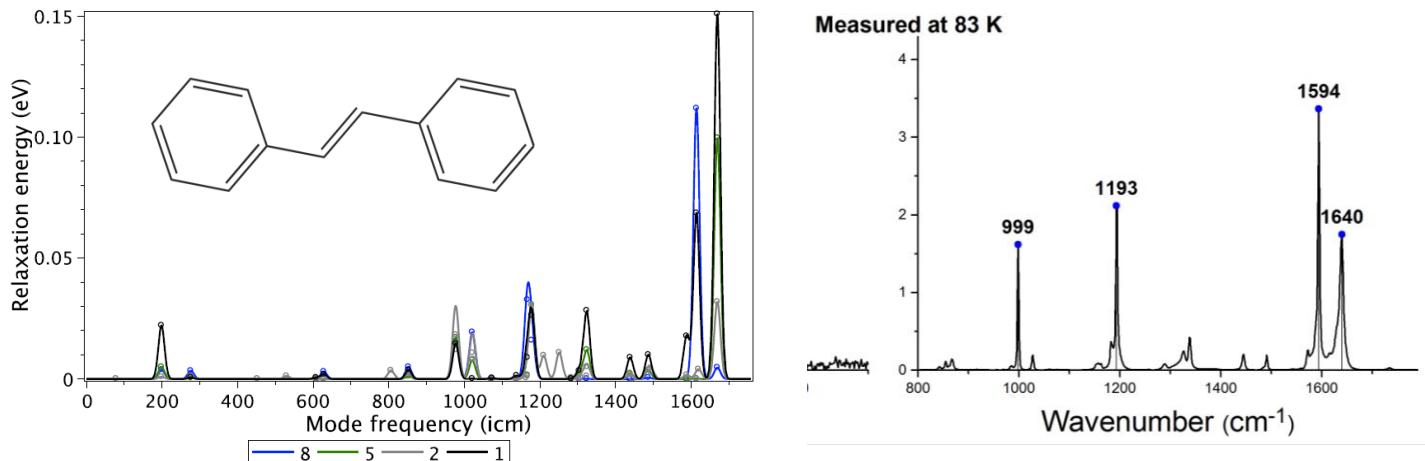
Simplest electron-phonon Hamiltonian (Holstein-Peierls):

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

here  $c_i$  – quasiparticles (excitons, holes etc.) described by coarse-grained Hamiltonian,  $b_\alpha$  – normal modes or phonons,

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

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



# Linear response

- Electric field polarizability, dielectric function
- IR and Raman intensities

# Batch calculations and benchmarking

- Batch calculations
- Benchmarking (as side task)

# Batch calculations

- Before starting batch calculations
  - Document computational protocol
  - Assess demands vs resources
  - If variation of runtimes in your set is large think about efficient processing
  - Maybe run a small subset
- During calculations
  - Check if everything goes smoothly
- After calculations
  - Identify failed jobs and decide what to do with them
  - Keep results in a well-maintained database to avoid repeated calculations
- If you use shared facilities
  - Remember that there are other users
  - Clean up after finishing or failures

# Benchmarking (as side task)

- Required for a new combination of system and method

## 1. Benchmarking against experiment:

- Use training and validation sets  
(e.g. geometry for training – spectra for validation)
- Use only reliable data for training
- In most cases you can avoid training by experiment  
(e.g. use Koopman's theorem or options 2,3)
- Always compare (validate) your calculations with experiment

## 2. Benchmarking against higher-level theory:

- Make sure that you use relevant property for comparison  
(e.g. it can be smallest molecule in series or easier-to-calculate property)

## 3. Compare several reasonably good methods:

- Always check sensitivity of your results to method
- Use range of methods expected to get lower and upper bounds  
(e.g. B3LYP and ωB97X for band gap of large π-conjugated molecules)

# Complex calculations

- Intermolecular interactions
- Solvent effects: implicit solvation and QM/MM
- Embedding and fragmentation methods
- Photoelectron spectroscopy (PES)
- Pump-probe spectroscopy
- X-ray Free-Electron Laser (XFEL)
- Nuclear magnetic resonance (NMR) spectroscopy

# Intermolecular interactions

- Use ‘plain’ DFT only if dispersion forces are small
- MP/CC can be used for fragment benchmarking
- Use [Symmetry-Adapted Perturbation Theory \(SAPT\)](#) for in-depth study, see also [DOI:10.1063/5.0005093](#)
- Dispersion-corrected DFT (DFT-D) such as [D3/D4](#) is the best “universal” approach for organic molecules
- Many-Body Dispersion (MBD) is one of the most reliable “post-DFT” methods
- Use nonlocal van der Waals density functional [vdW-DF2](#) if analytic derivatives are needed

*See also* [Review by Hermann&Tkachenko](#)

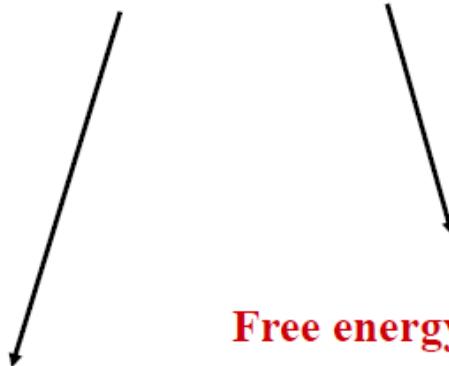
# Solvent effects (from Jensen)

- Non-specific (long-range) solvation
  - Polarization
  - Dipole orientation
- Specific (short-range) solvation
  - Hydrogen bonds
  - van der Waals interaction
  - Solvent shell structure
  - Solvent–solute dynamics
  - Charge transfer effects
  - Hydrophobic effects (entropy effects).

# Solvation energies and models

- $\Delta G_{\text{sol}} \Rightarrow$  the free energy change to transfer a molecule from vacuum to solvent.
- $\Delta G_{\text{sol}} = \Delta G_{\text{elec}} + \Delta G_{\text{vdw}} + \Delta G_{\text{cav}}$

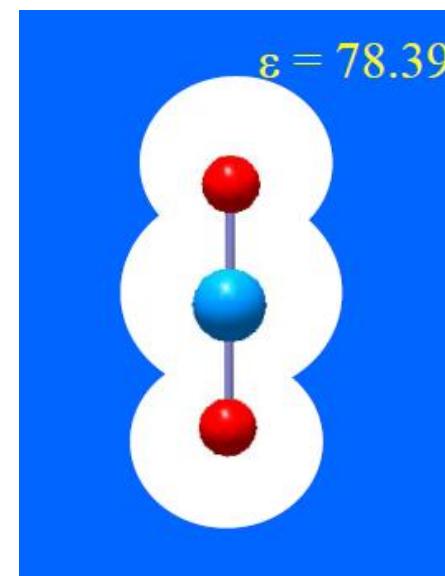
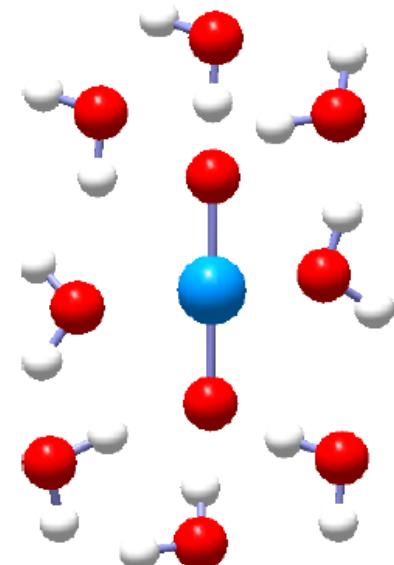
Electrostatic component



Van der Waals interaction between solute and solvent

Free energy required to form the solute cavity. Is due to the entropic penalty due to the reorganization of the solvent molecules around the solute and the work done in creating the cavity

- Explicit solvent models
- Implicit solvent models



# Solvent effects – explicit solvation

Quantum Mechanics/Molecular

Mechanics (QM/MM)

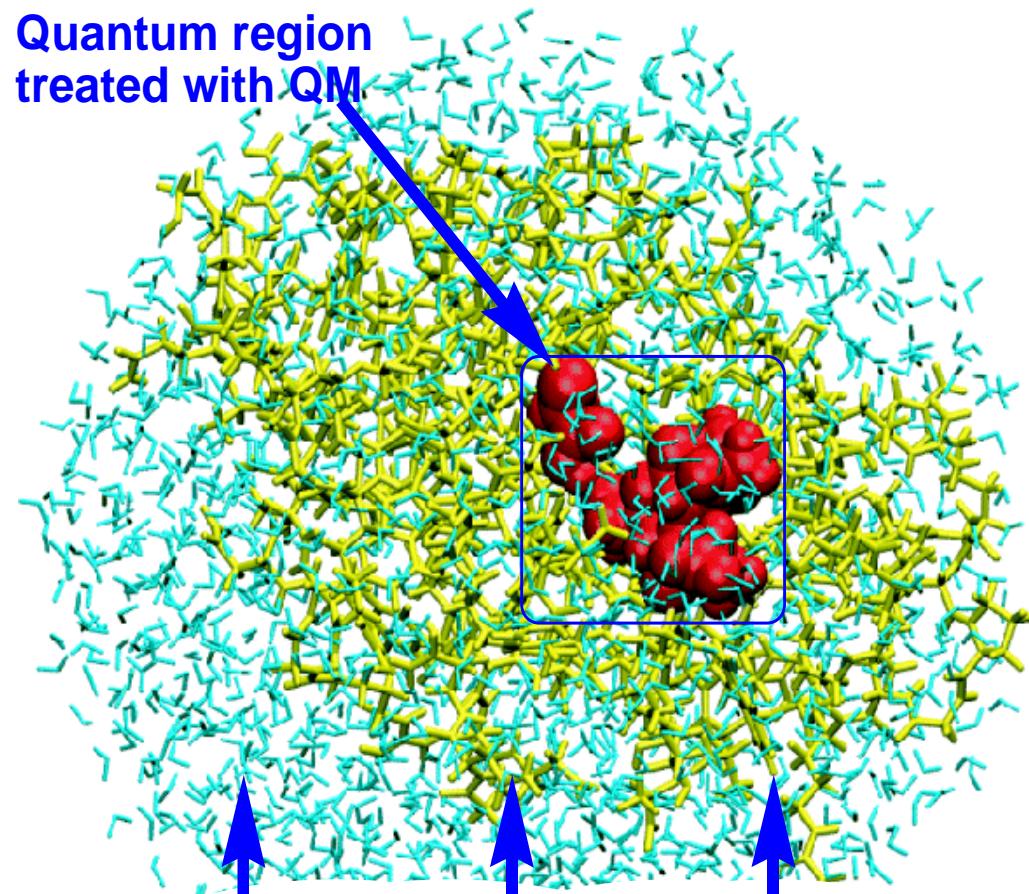
Also Morokuma's ONION (layered structure, complexity reduces when going from the center to periphery)

The simplest case is to add a few 'solvent molecules' around your target system.



Be careful! The solvent molecules have to be 'intelligently' put around the solute, where interactions matter the most (e.g., hydrogen bonding).

Quantum region  
treated with QM



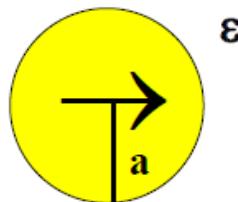
Solvent, protein, etc. treated  
with MM. Interacts with QM

# Solvent effects – implicit solvation

- Solvent is treated as a polarizable continuum with a dielectric constant,  $\epsilon$ , instead of explicit solvent molecules.
- The charge distribution of the solute polarizes the solvent producing a reaction potential.
- The reaction potential of solvent alters the solute.
- This interaction is represented by a solvent reaction potential introduced into the Hamiltonian.
- Must be computed self consistently
- Also know Interactions as self consistent reaction field (SCRF) methods
- Significantly cheaper than explicit solvent models
- Cannot model specific interactions such as hydrogen bonds

## *Example the Onsager model:*

**Onsager (1936):** a polarizable dipole at the center of a sphere. The solute dipole induces a reaction field in the surrounding medium which in turn induces an electric field in the cavity (reaction field), which interacts with the dipole: analytic solution



$$\phi_{RF} = \frac{2(\epsilon - 1)\mu}{(2\epsilon + 1)a^3}$$

Energy of a dipole in an  $\bar{E}$  field  $\phi_{RF} = -\phi_{RF}\mu$

Work done assembling charge distribution  $= \frac{\phi_{RF}\mu}{2}$

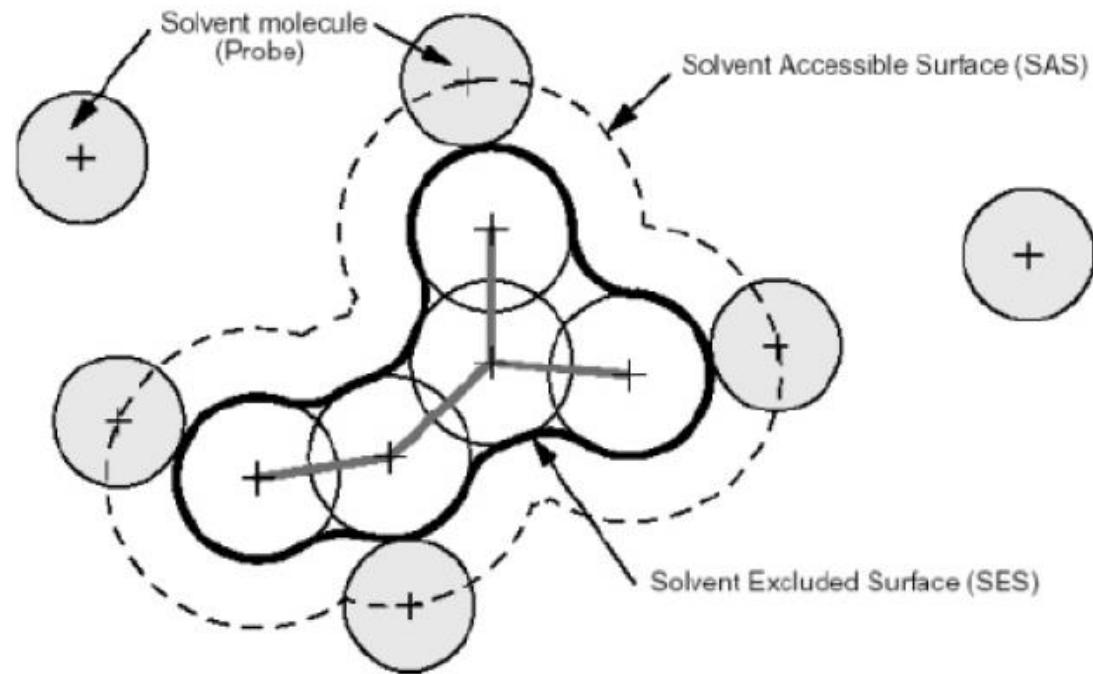
$$\Delta G_{elec} = \frac{-\phi_{RF}\mu}{2} = -\frac{(\epsilon - 1)\mu^2}{(2\epsilon + 1)a^3}$$

# Implicit solvation: practical models

- **Realistic molecular cavity;**
- **Solve Poisson equation in some approximation numerically:**

$$\nabla \cdot (\epsilon(\mathbf{r}) \nabla \phi(\mathbf{r})) = -4\pi\rho(\mathbf{r})$$

a second-order differential equation describing the connection between the electrostatic potential  $\phi$ , the charge distribution  $\rho$  and the dielectric constant  $\epsilon$



- The Polarizable Continuum Model (PCM) employs a van der Waals cavity formed by interlocking atomic van der Waals radii scaled by an empirical factor, a detailed description of the electrostatic potential, and parameterizes the cavity/dispersion contributions based on the surface area.
- The COnductor-like Screening MOdel (COSMO) also employs molecular shaped cavities, and represents the electrostatic potential by partial atomic charges.

**Bottom line: magic words – SCRF, PCM, COSMO and dielectric constant!**

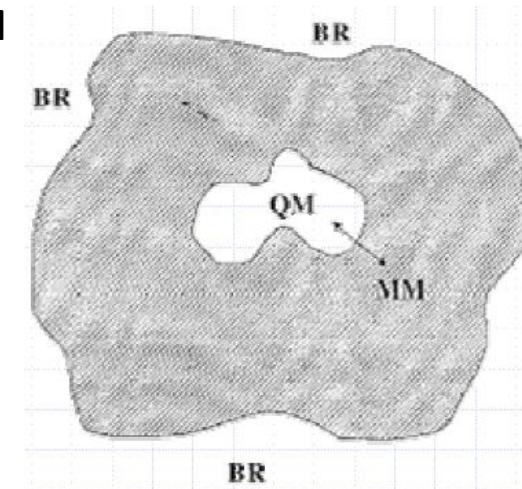
# QM/MM – a standard tool

## QM/MM Partitioning

$$E = E_{QM} + E_{MM} + E_{QM/MM}$$

- What should be used in the QM region? Ab Initio OR DFT OR Semiempirical
- QM/MM interaction term can be problematic – it is not good to have this boundary close to the chemistry of interest...
- Not clear which force fields to use – much experience with expected accuracy of ab initio methods alone and MM methods alone, but not much with QM/MM
- No direct map from wavefunction to parameters

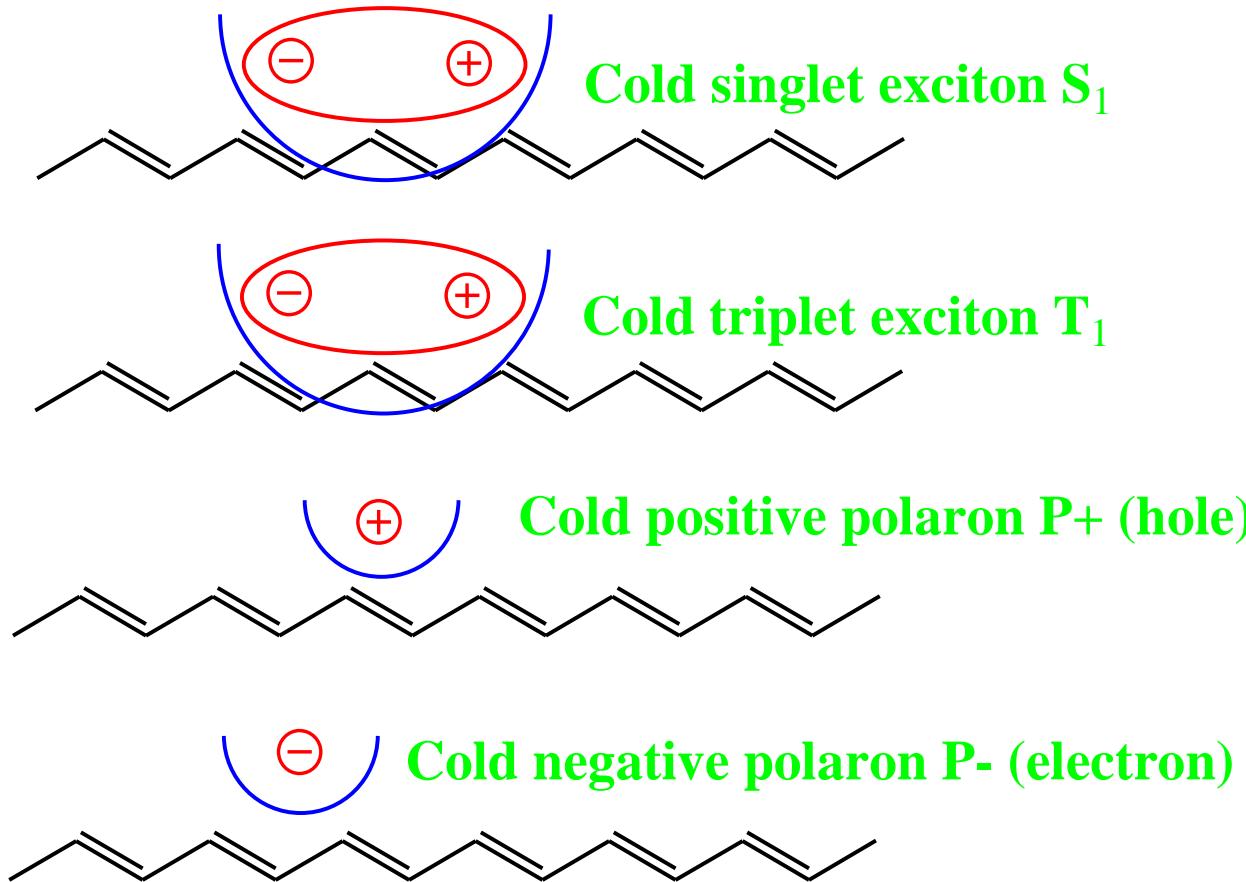
$$\begin{aligned} V(\vec{R}) = & \sum_{i \in bonds} k_{i,bond} \left( r_{i,bond} - r_{i,bond}^{eq} \right) + \sum_{i \in angles} k_{i,angle} \left( \theta_{i,angle} - \theta_{i,angle}^{eq} \right) + \\ & + \frac{1}{2} \sum_{\substack{i \neq j \\ i, j \in atoms}} \frac{q_i q_j}{|r_i - r_j|} + \frac{1}{2} \sum_{\substack{i \neq j \\ i, j \in atoms}} V_{LJ}^{\bar{ij}} \left( |r_i - r_j| \right) \end{aligned}$$



- Mechanical Embedding: Include only Van der Waals in  $E_{QM/MM}$
- Electrostatic Embedding: Include electrostatic interaction in  $H_{QM/MM}$  Electrostatic potential fitting
- Covalent Embedding: Breaking the bond at the QM/MM borderline. Most difficult scheme. Need to assure continuity of the energy. Electronegativity idea (Thiel). Frozen orbital idea.

# Example: spatial extent of relaxed excitations

I. H. Nayyar, E.R. Batista, A. Saxena, D. L. Smith, R. L. Martin, S. Tretiak, J Phys Chem Lett 2, 566 (2011)

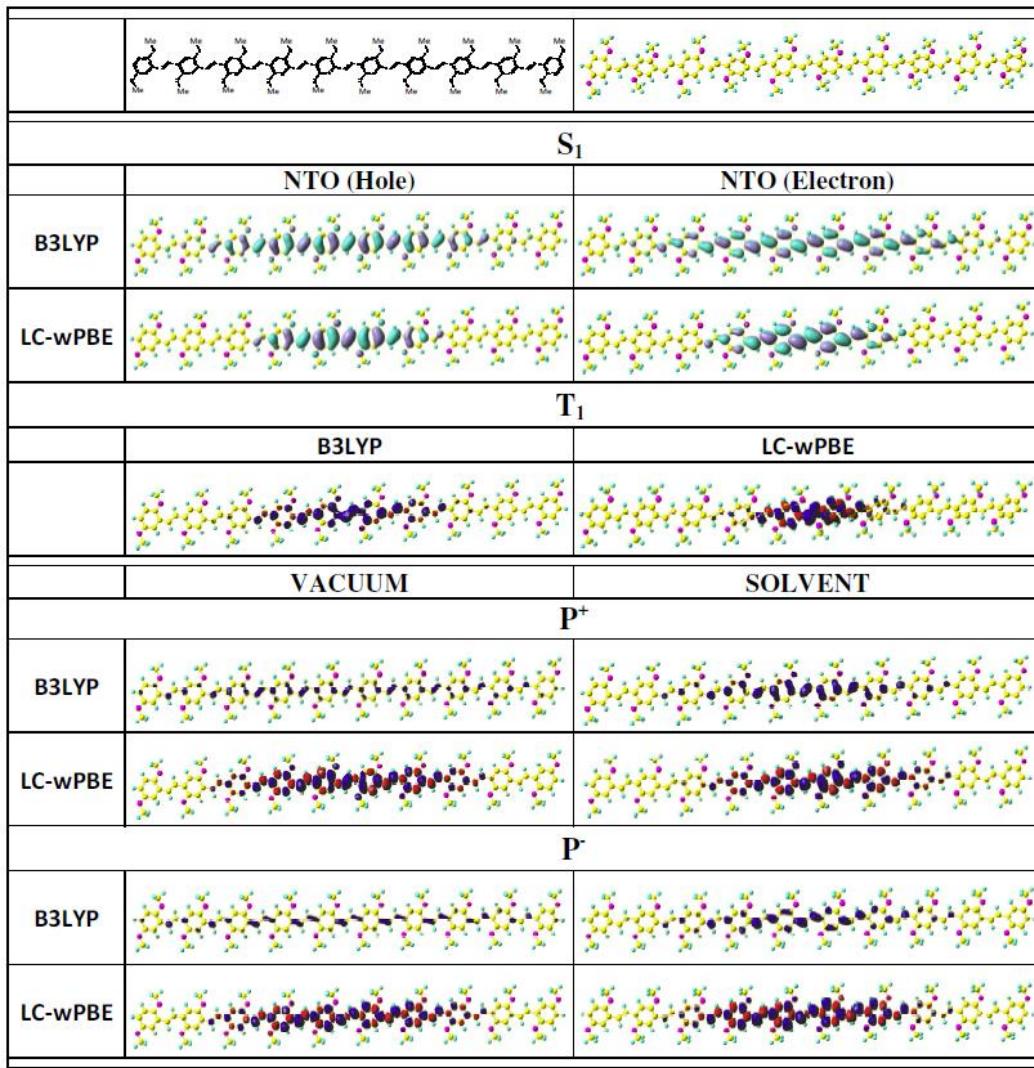


**Main questions:**

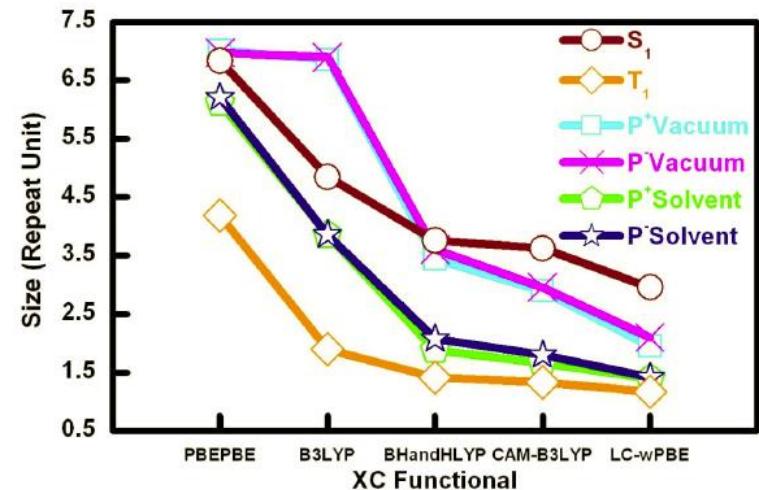
- a) Dependence on the DFT model
- b) The role of the dielectric medium

Experimental determination of polaronic size in MEH-PPV : ~10 C-H units ~ 2-3 repeat units

# ... all excitations are localized

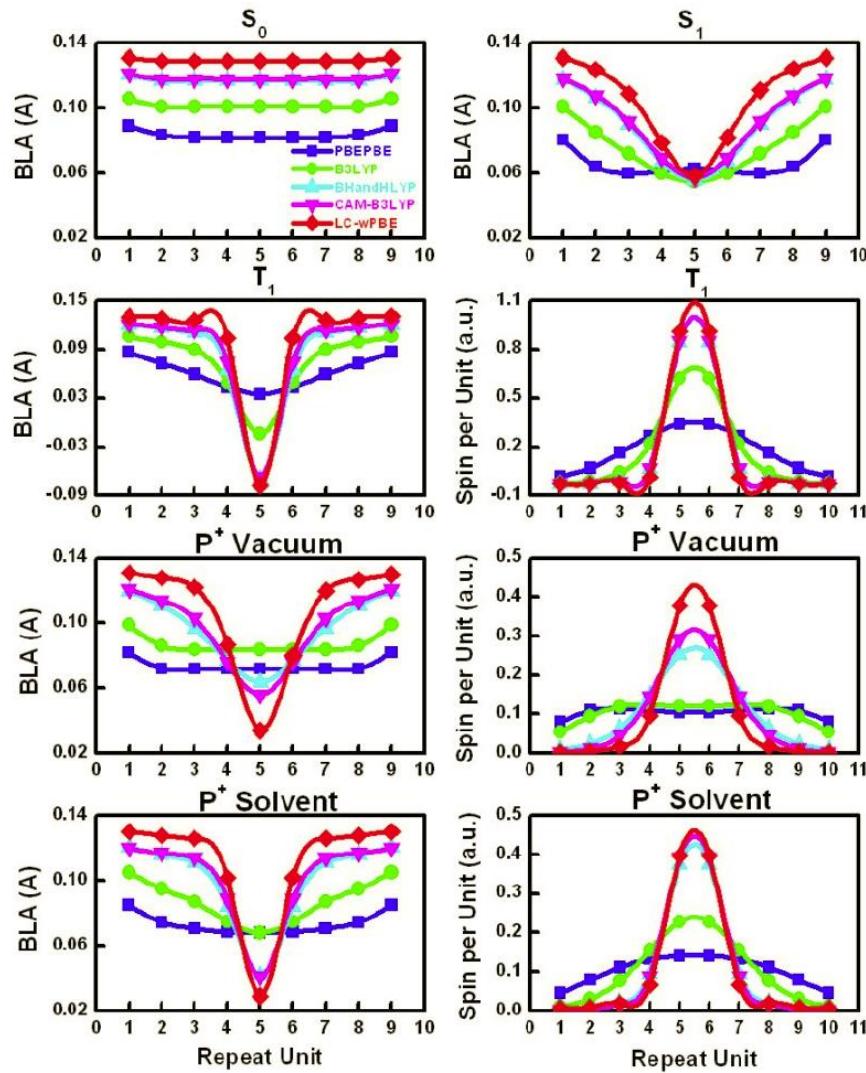


Orbital plots show natural transition orbitals (NTOs) for hole and electron for  $S_1$  and Mulliken atomic spin density distribution for  $T_1$ ,  $P^+$  and  $P^-$  calculated at B3LYP/6-31G\* and LC-wPBE/6-31G\* optimized levels.



Characteristic size of the electronic excitation defined as full width at half maximum (in terms of repeat units).

# ... variations of bond lengths and spin densities



Orbital exchange in the DFT models

- a) PBE (0%)
- b) B3LYP (20%)
- c) BHandHLYP (50%)
- d) CAM-B3LYP (20-65%)
- e) LC-wPBE (0-100%)

Moderate polarity solvent (COSMO model)

Bond length alternation (BLA) (Å) and Mulliken atomic spin densities (a.u.) per repeat unit of MEH-PPV oligomer computed with 6-31G\* basis set.

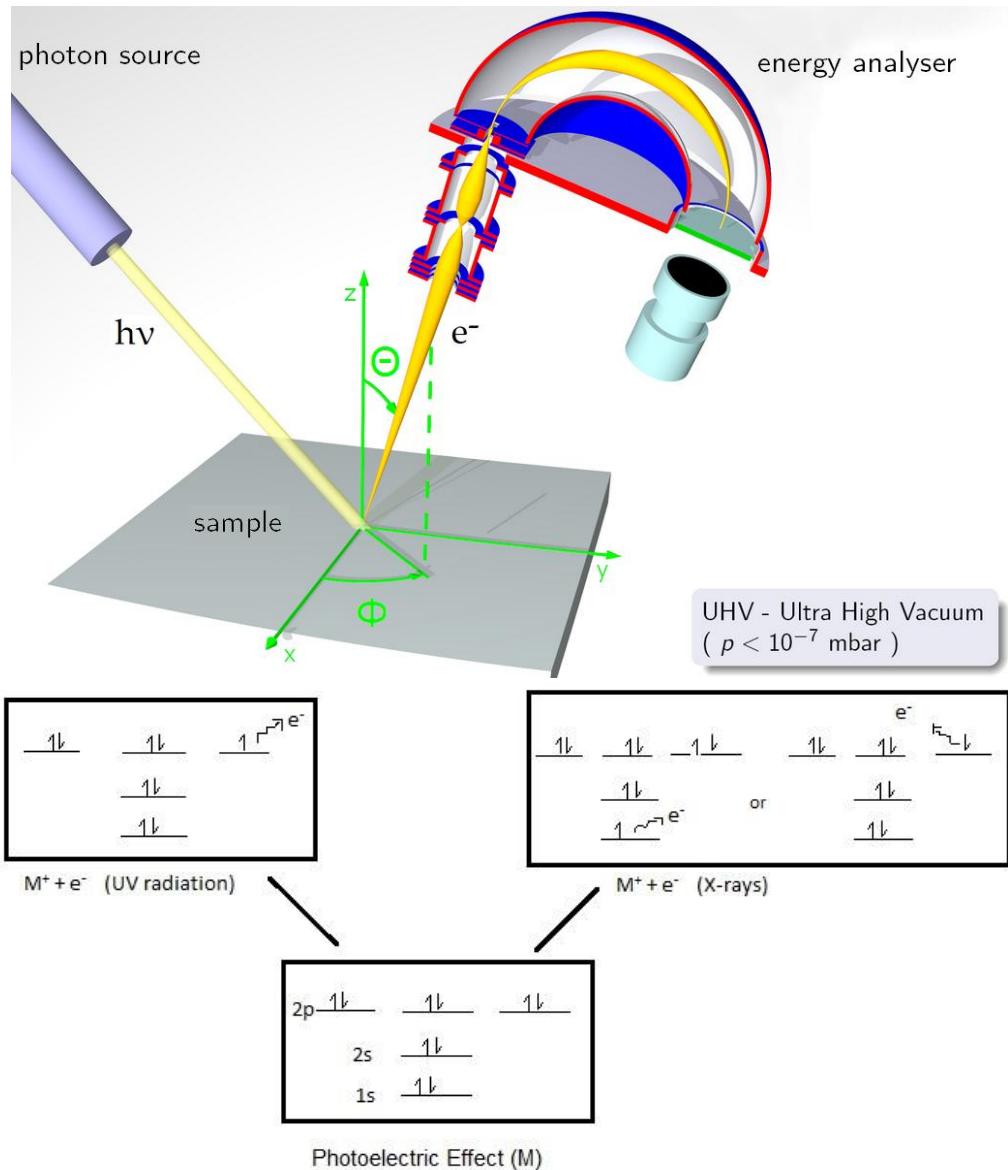
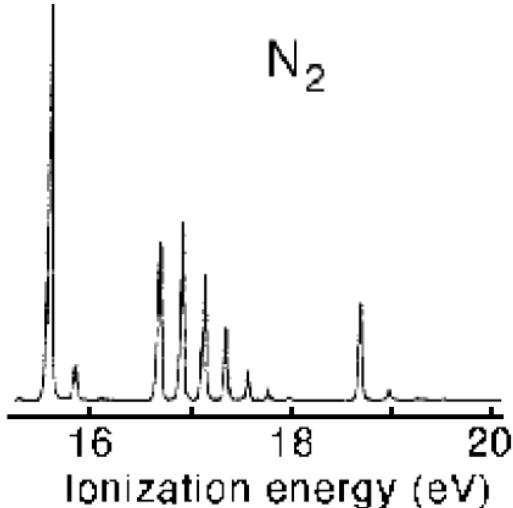
# Photoelectron spectroscopy (PES)

Come in variations:

Ultraviolet Photoelectron Spectroscopy (UPS) and X-ray Photoelectron Spectroscopy (XPS)

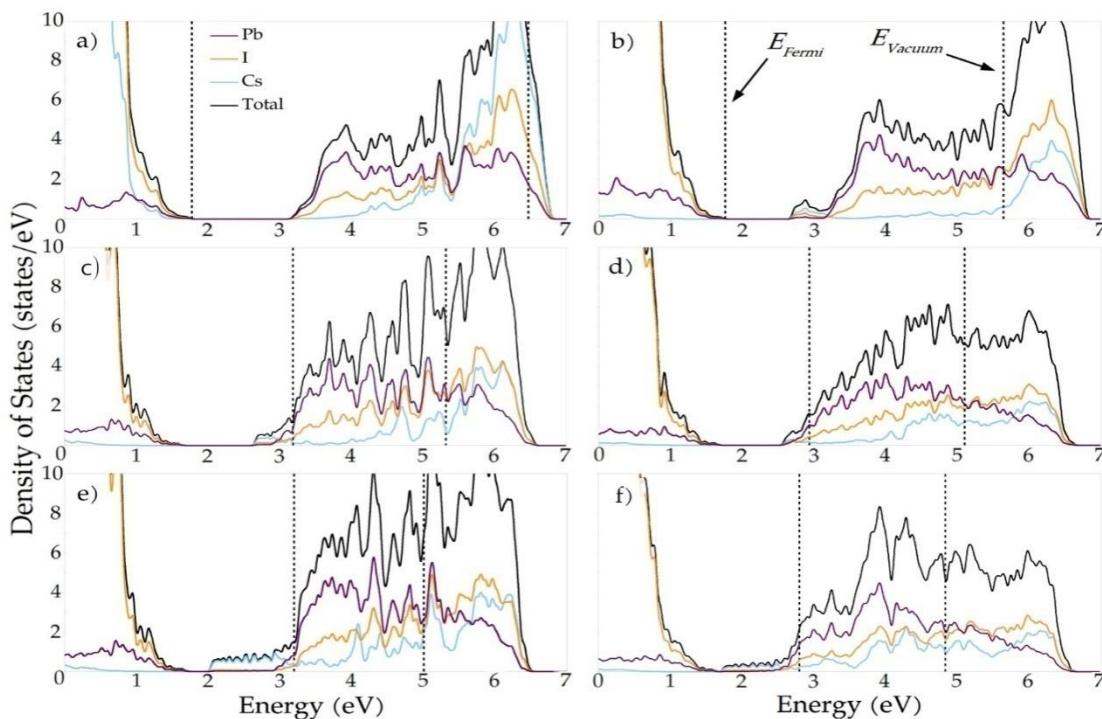
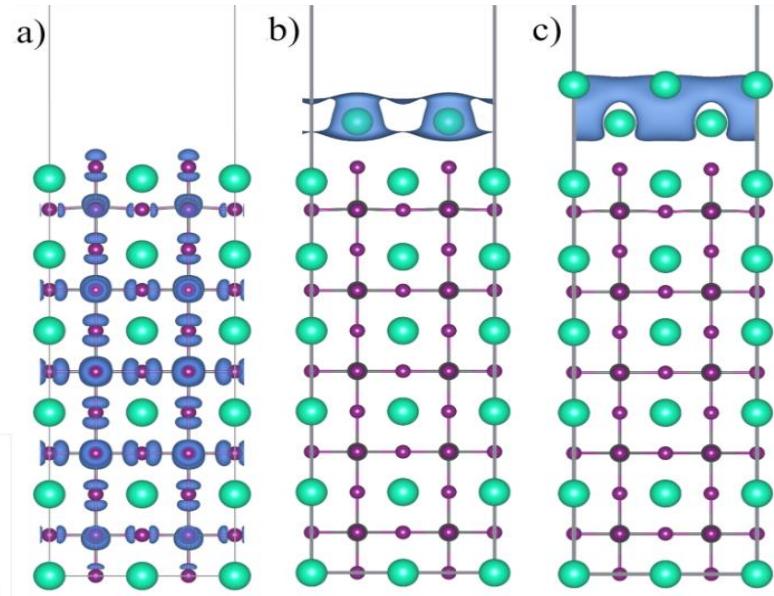
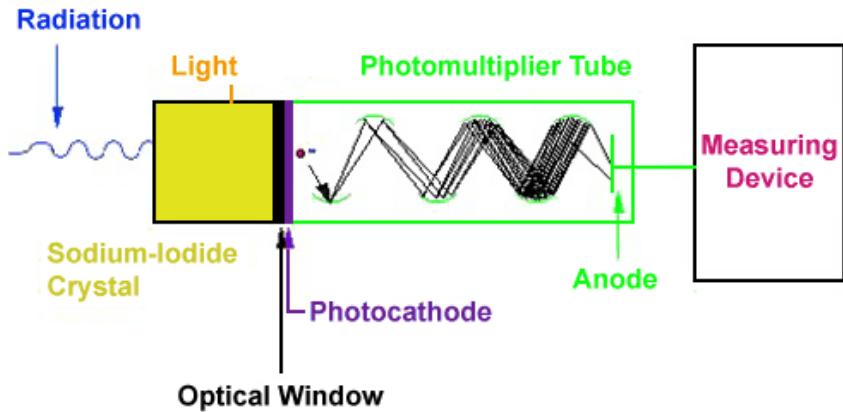
$$E_k = h\nu - \text{IP} \quad (\text{i})$$

To calculate PES peaks one needs to evaluate energy levels occupied by electrons



# Case study: photocathodes

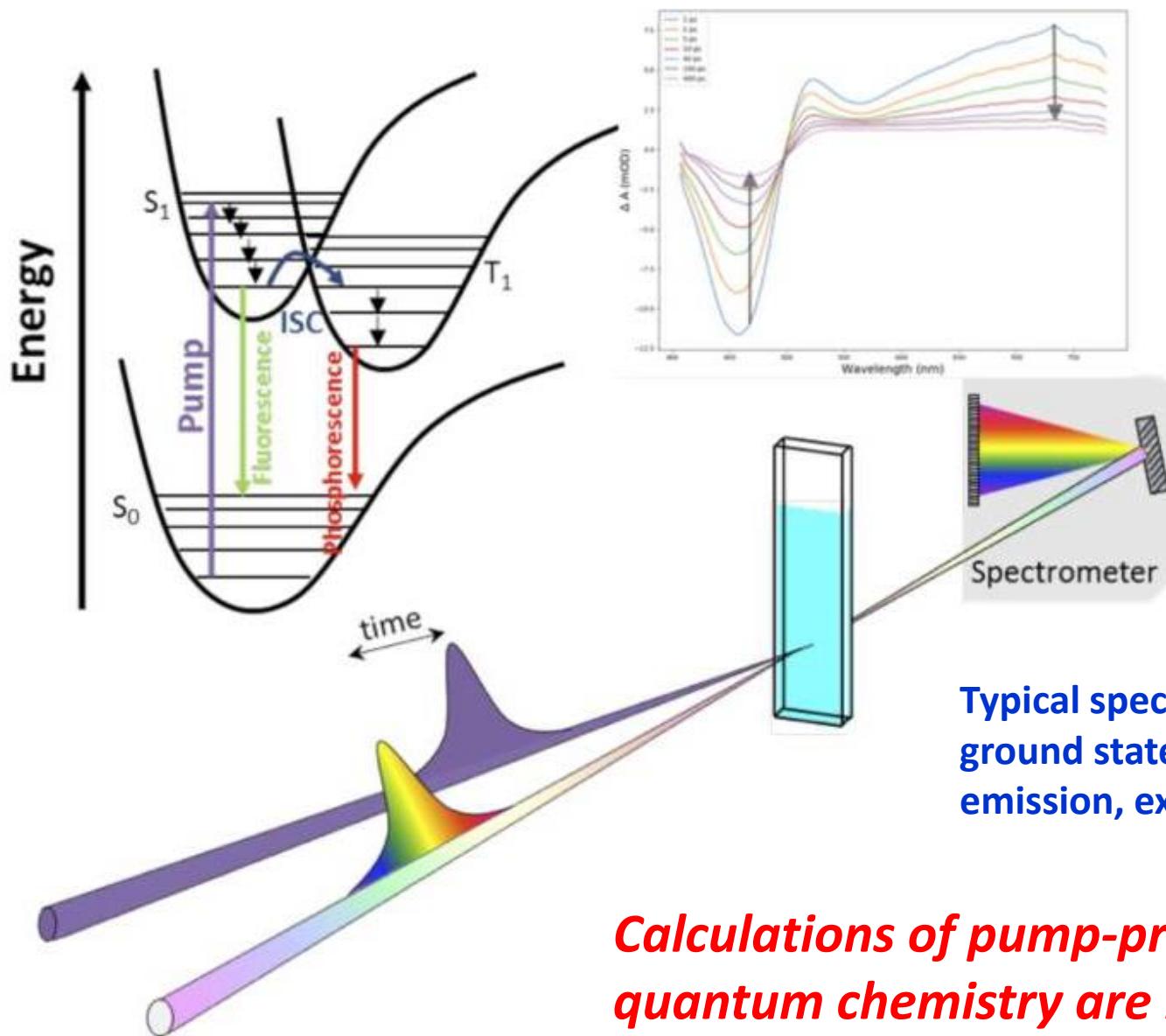
*Requirements: low work-function and high yield*



Halide perovskite materials (such CsPbBr<sub>3</sub>) coated with Cs have lower work functions (from 4.5 eV to ~2 eV, theory) and a high yield of photoelectrons (unpublished)

# Pump-probe (transient absorption) spectroscopy

*A major tool to probe an electronic dynamics in materials*

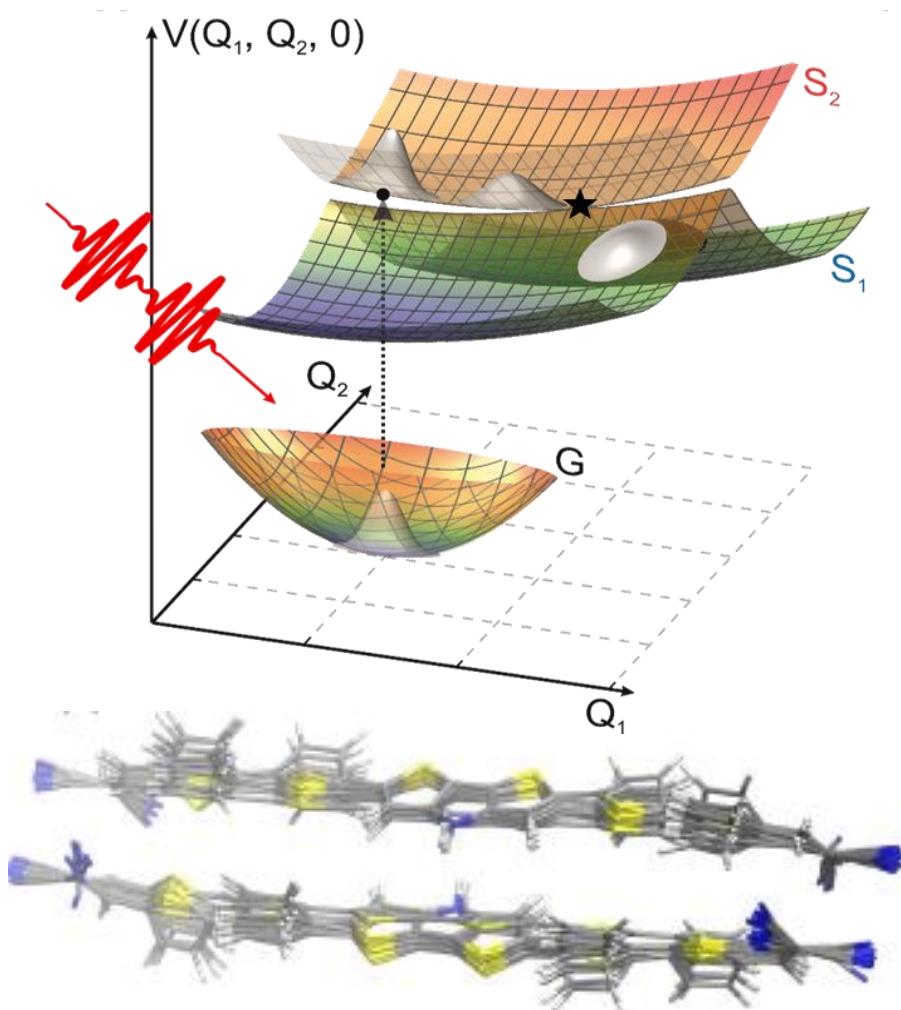


Dynamical information is extracted from time-evolution of various peaks in transient absorption spectra

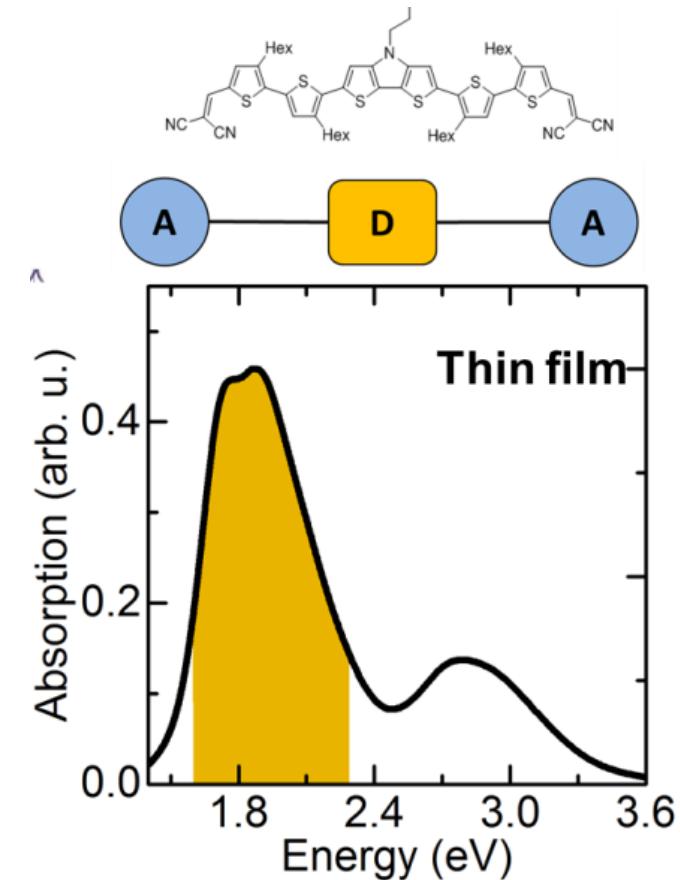
Typical spectroscopic features:  
ground state bleach, stimulated emission, excited state absorption

*Calculations of pump-probe spectra using quantum chemistry are non-trivial*

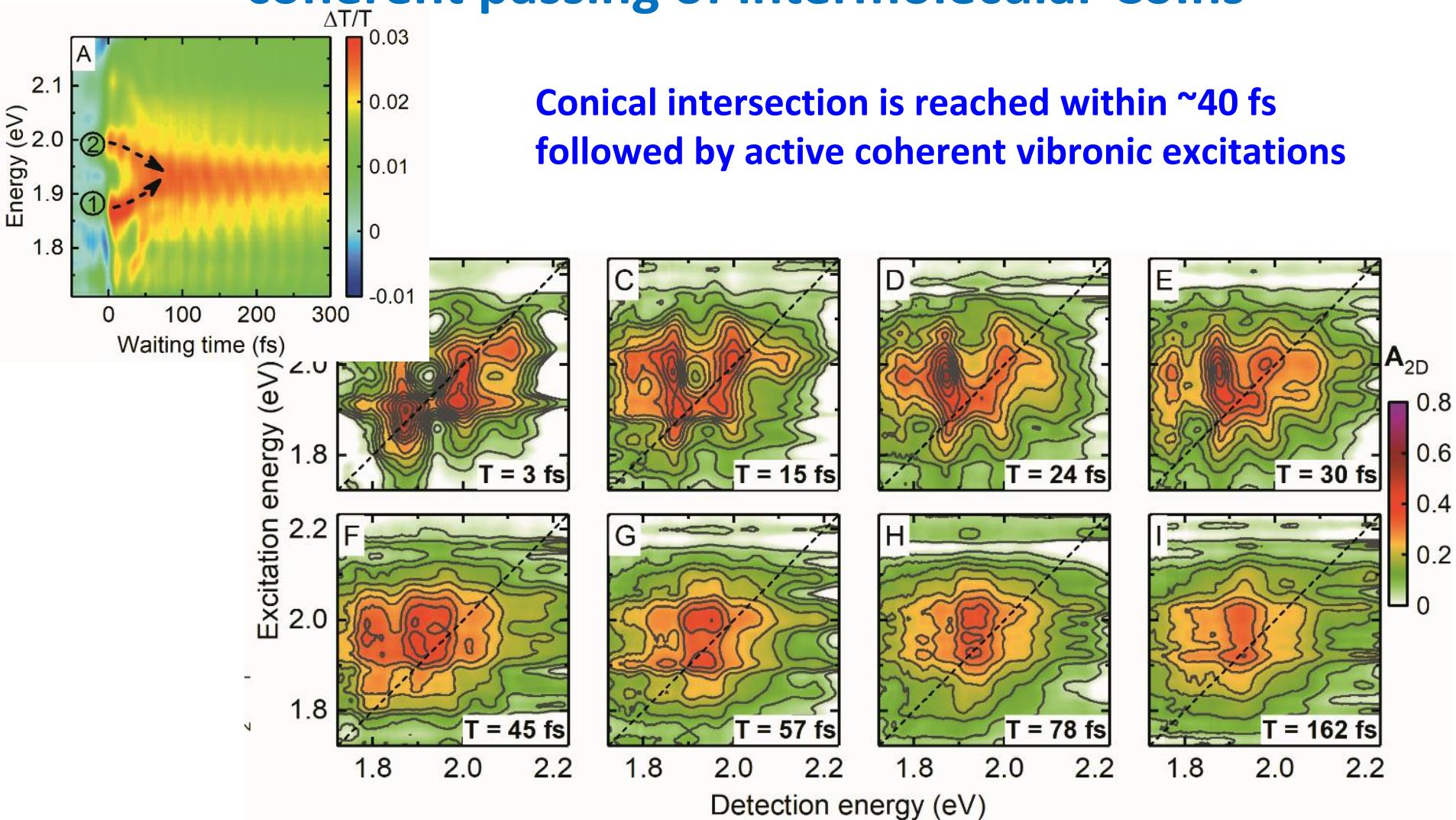
# Case study: Intermolecular energy transfer through intermolecular conical intersection in organic photovoltaics



Experimental observation of coherent vibrational dynamics in thin film



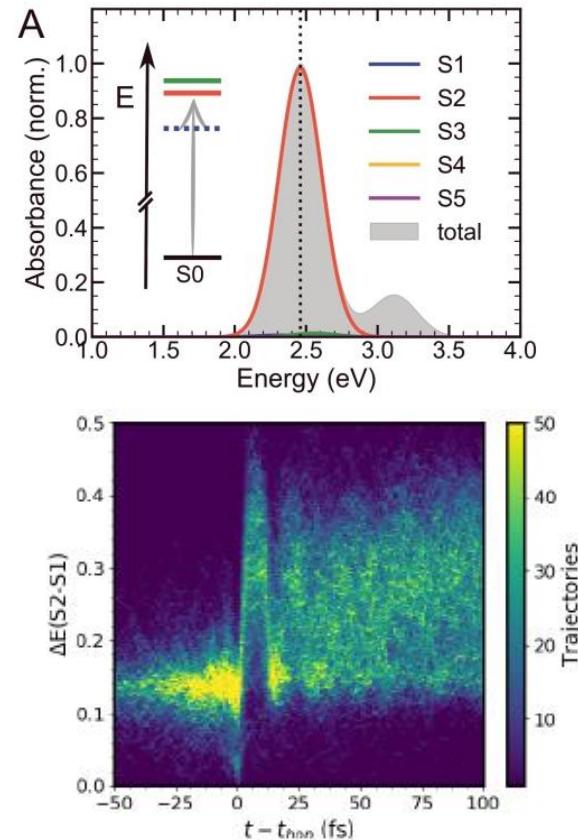
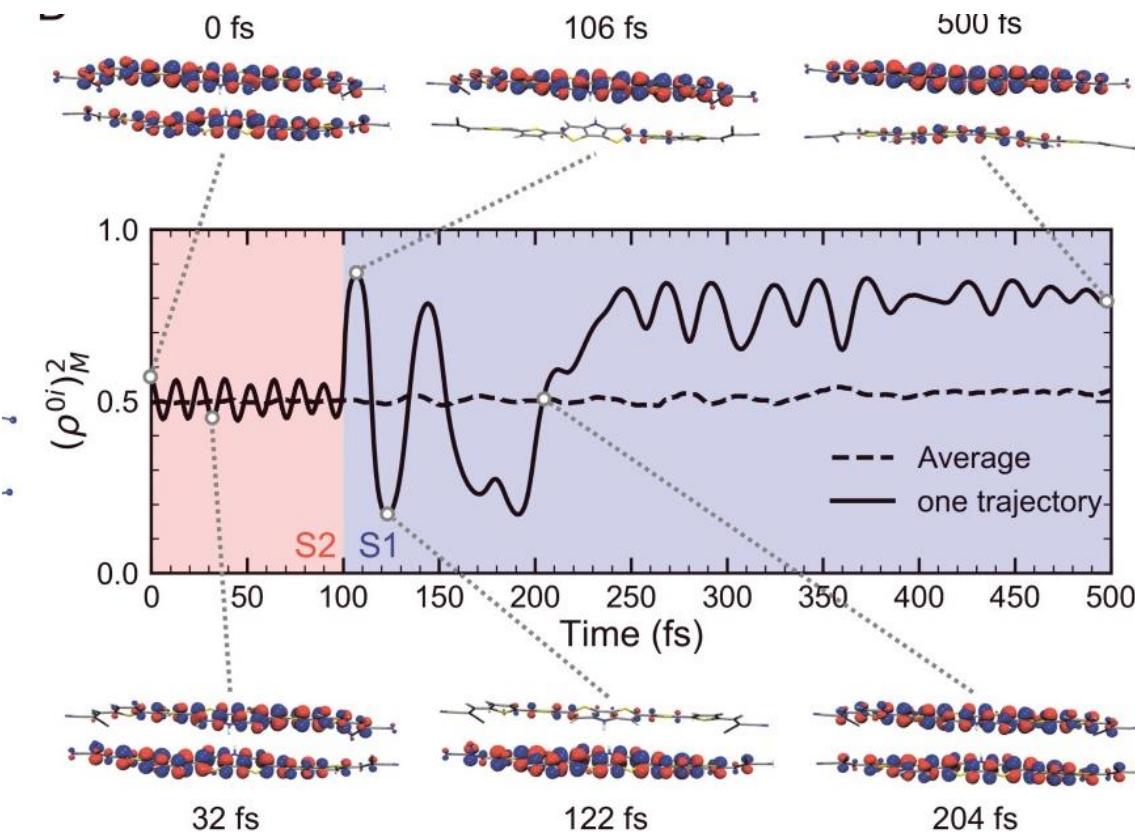
# Case study: Two-dimensional electronic spectra suggest coherent passing of intermolecular Colns



A. De Sio, E. Sommer, X. T. Nguyen, L. Gross, D. Popović, B. Nebgen, S. Fernandez-Alberti, S. Pittalis, C. A. Rozzi, E. Molinari, E. Mena-Osteritz, P. Bäuerle, T. Frauenheim, S. Tretiak, C. Lienau, *Nature Nanotech.* (2020, <https://doi.org/10.1038/s41565-020-00791-2>)

# Case study: Modeling of coherent non-adiabatic dynamics in a molecular dimer (H-aggregate)

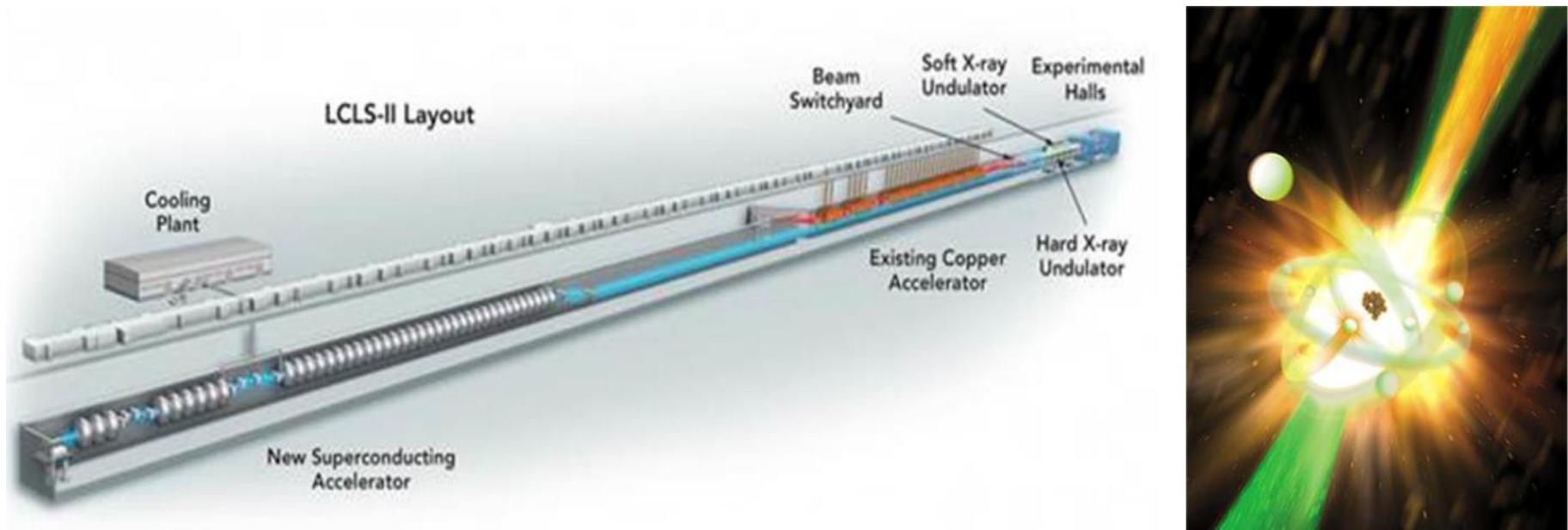
Intermolecular conical intersection is reached within 100 fs. Excess of electronic energy excites vibrational modes coupled on upper and lower surfaces (modulation of dynamics), the wavefunction “collapses” (self-trapping).



A. De Sio, E. Sommer, X. T. Nguyen, L. Gross, D. Popović, B. Nebgen, S. Fernandez-Alberti, S. Pittalis, C. A. Rozzi, E. Molinari, E. Mena-Osteritz, P. Bäuerle, T. Frauenheim, S. Tretiak, C. Lienau, *Nature Nanotech.* (2020, <https://doi.org/10.1038/s41565-020-00791-2>)

# X-ray Free-Electron Laser (XFEL)

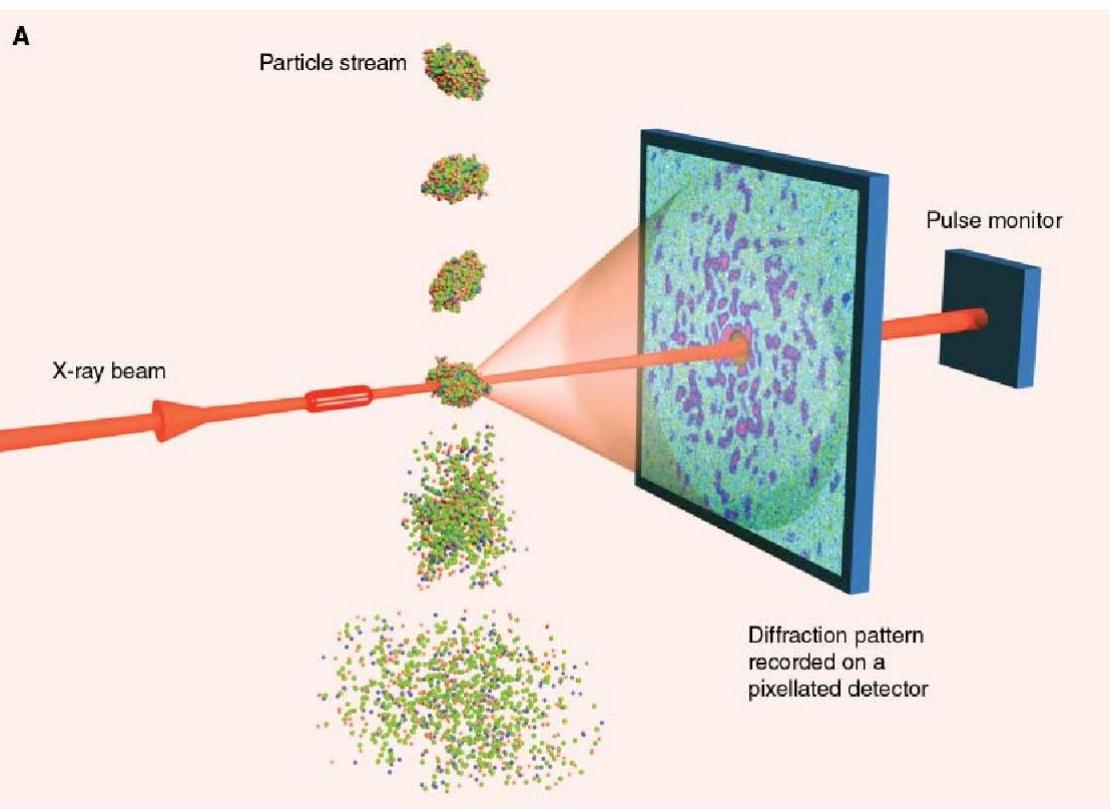
## Current and planned XFEL capabilities for LCLS (Stanford)



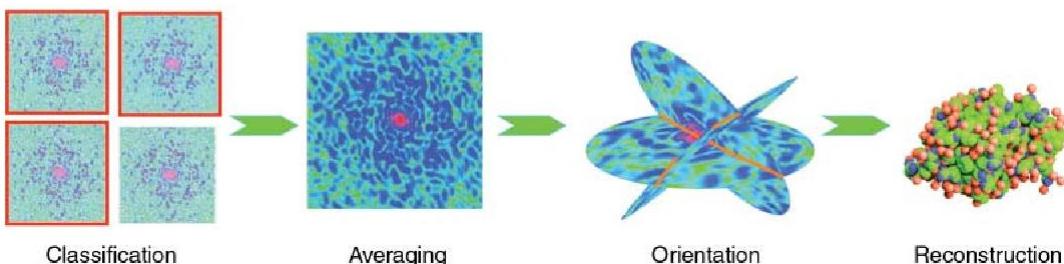
XFELs (shown for LCLS-II) generate intense x-ray pulses using electrons accelerated to highly relativistic speeds. LCLS operates, for example, at an energy of 15 billion electron volts, producing electrons traveling at 99.999999% of the speed of light. These electrons are passed through periodically modulated magnetic fields, the so-called undulators. The undulators accelerate the electrons and induce them to emit x-ray photons. At the same time, interactions between electrons, the undulator's magnetic fields, and emitted x-ray photons cause the electrons to bunch together in periodic structures. The electrons then radiate coherently in phase with one another, corresponding to laser emission. This coherent emission process can lead to extremely intense and short pulses of x-rays. It is possible to produce x-rays with peak brightness more than 10 million times greater than the brightest modern x-ray storage ring facility, as shown interacting with matter.

# Single molecule structure resolution with XFEL

A



B



XFELs impact:

- Probing and controlling electron motion within a molecule;
- Discovering novel quantum phases through coherent light-matter coupling
- Capturing rare events and intermediate states in the transformation of matter

***RF being one of shareholders (and Skoltech) has a priority access to European X-Ray Free-Electron Laser Facility (European XFEL)***

Fig. 7 Schematic depiction of single-particle coherent diffraction imaging with an XFEL source. (A) The intensity pattern

# Discussion (short)

1. What is the difference between vertical and adiabatic transitions?
2. For which state solvent effects are the strongest: S<sub>0</sub> (zero charge), S<sub>1</sub>, T<sub>1</sub>, cation?
3. Often only IP is available in cyclic voltammetry, so experimentalists add band gap estimated from UV-Vis absorption spectra to get EA (they call them HOMO and LUMO energies). What is true meaning of thus obtained LUMO energy?

# Discussion (less trivial)

1. What HOMO should be taken in Koopman's theorem: of neutral or ionized state? What can we say about  $\text{EA}_{\text{vert}} + E(\text{LUMO})$ ?
2. Upon (dis)charging metal-ion electrode some peaks in Raman spectra (dis)appear. Does this mean (dis)appearance of vibrational modes or vibronic couplings?
3. Why for PES, e.g. work-function for electrons in photocathodes, the surface dipole matters?