Summer 2019

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Outline

- Background
  - Electronics & Photonics
  - Electro-optics
  - Computational Chemistry
  - Quantitative Structure-Property Relationships (QSPR)
- Datasets and Studies
- Future Work

Electronics

- Fundamentally, devices that use electrons to process and transmit data
- Hence, electronics
- Ex: computers/calculators
- Size: ~ 10s of nanometers
- Speed:
- Energy Cost:

Photonics

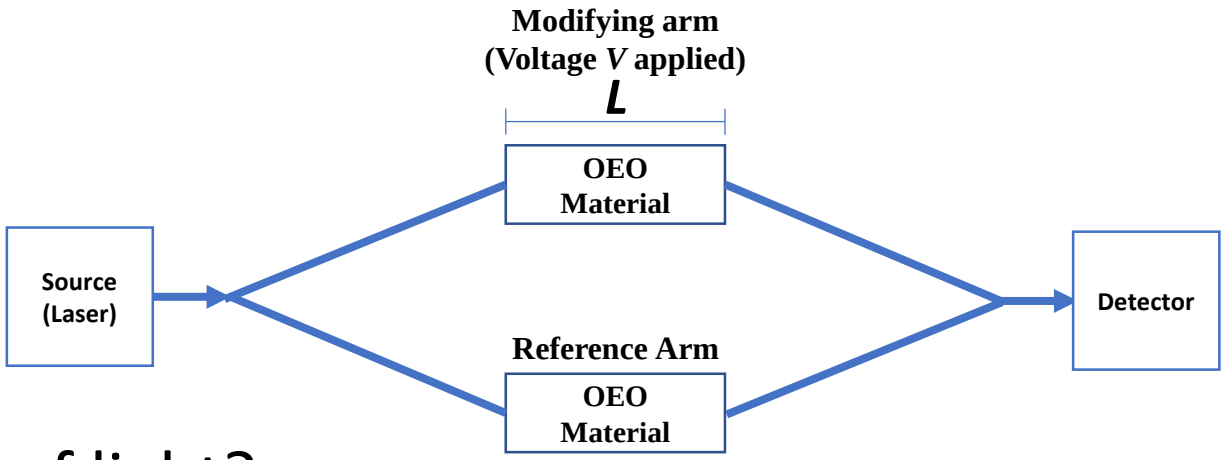
- Fundamentally, devices that use photons to process and transmit data
- Hence, photonics
- Ex: fiber-optic cables
- Size: ~ Xs of __meters
- Speed:
- Energy Cost:

Electro-optics

- Nonlinear Optical Effects
  - Generally: Polarization density **P** responds non-linearly to electric field |**E**| of incident light
    - Pockels Effect: Nonlinear electro-optic effect in which an applied electric field changes the index of refraction of a material $\Delta n = \frac{n^3 r_{33} |\boldsymbol{E}|}{2}$
      - $|\boldsymbol{E}|$: Magnitude of applied electric field
      - r_{33}: Electro-optic coefficient. $r_{33} \propto N\beta\langle cos^3\theta\rangle$ (Want to maximize!)
        - N: Chromophore concentration
        - β: Molecular hyperpolarizability
        - $\langle cos^3\theta\rangle$: Acentric order parameter

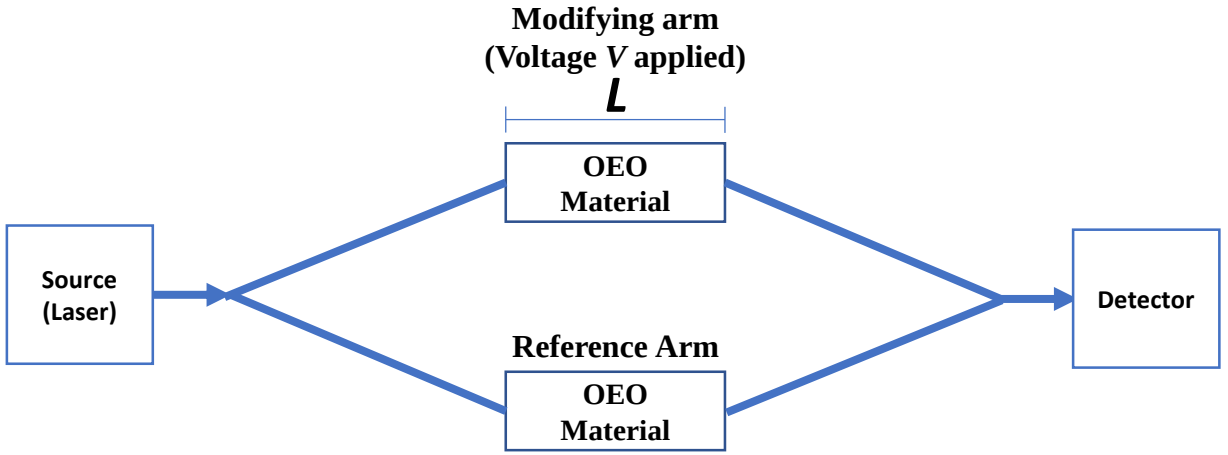
        } Properties of importance!

Electro-optics



- How to encode 0s and 1s on a wave of light?
  - Operation of a Mach-Zehnder Modulator:
    1. Inputted light is split equally into two arms of equal length
    2. In the modifying arm of length *L*, an applied voltage *V* changes the index of refraction of the OEO material by Δn (according to the Pockels effect), which changes the speed of the wave as it travels through the arm
    3. In the reference arm of the same length, light travels through the same OEO material, but without an applied voltage, so n is unchanged
    4. Waves from the arms recombine. The modulator is set up such that, with an applied field, waves combine 180° out of phase, resulting in complete destructive interference (binary 0). Without the field, waves have equal speed, combining in-phase (binary 1)

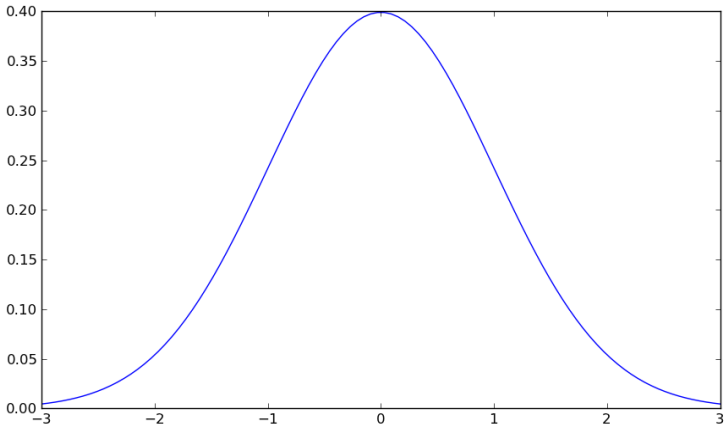
Electro-optics



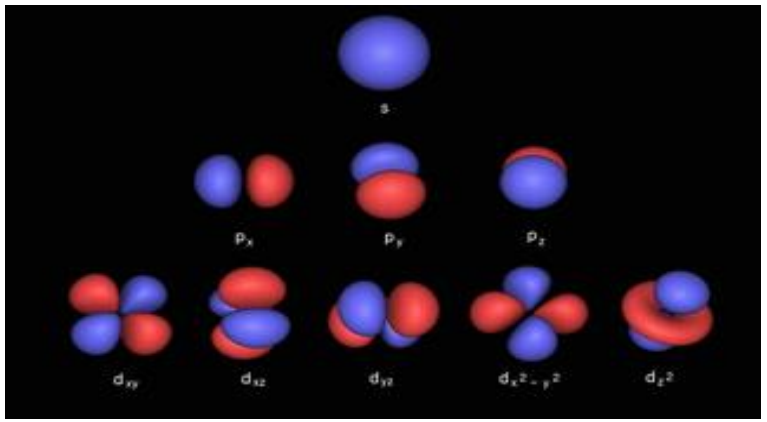
- Goal: Chip-scale modulators working at typical electronics voltages
  - $V_\pi L$: Voltage-length product, i.e. the waveguide length required for a 180° phase shift in the period of the light at a given voltage
    - We want to minimize $V_\pi L$
    - Recall the Pockels effect: $\Delta n = \frac{n^3 r_{33} |\boldsymbol{E}|}{2}$, $r_{33} \propto N\beta\langle cos^3\theta\rangle$
    - So we want to maximize N, β, and $\langle cos^3\theta\rangle$!

Computational Chemistry

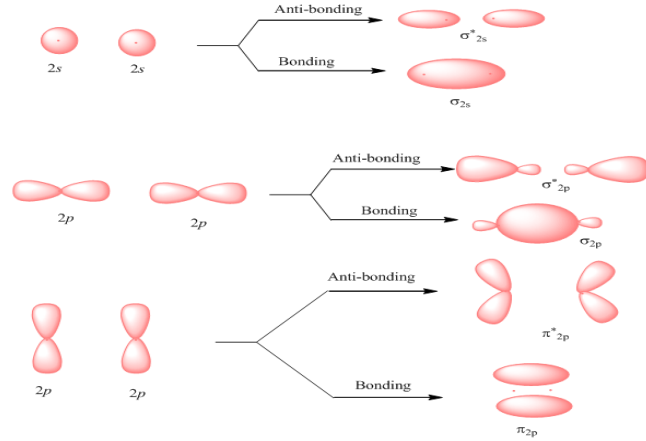
- Applying approximations to allow for mathematical calculations of molecular energies, properties, e.t.c.
- Molecular Orbital Theory
  - Delocalized description of chemical bonding
  - Linear Combination of Atomic Orbitals (LCAO)
    - Approximation that describes molecular orbitals as linear combinations of atomic orbitals, which are typically described as linear combinations of Gaussians



Gaussians



Atomic Orbitals



Molecular Orbitals

Computational Chemistry

- Atomic Orbital Approximations
  - Slater Type Orbitals: Accurate but expensive
    - Direct physical interpretation
    - Obey necessary conditions (Cusp condition & exponential decay)
    - Integrals are computationally expensive
  - Gaussian Orbitals: Cheap but inaccurate
    - No physical interpretation
    - No cusp condition, incorrect decay
    - Integrals are orders of magnitude cheaper due to the simplicity of the Gaussian function

Computational Chemistry

- How can we get the benefits of Slater-like orbitals without their painful integrals?
  - Answer: Linear Combinations of GTOs to approximate STOs

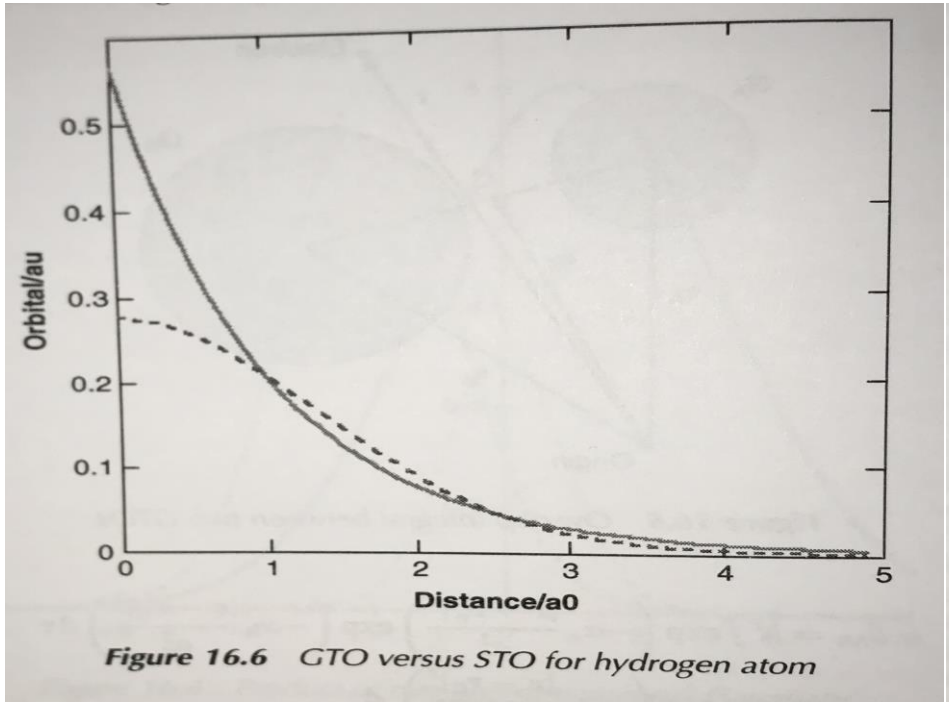


Figure 16.6 *GTO versus STO for hydrogen atom*

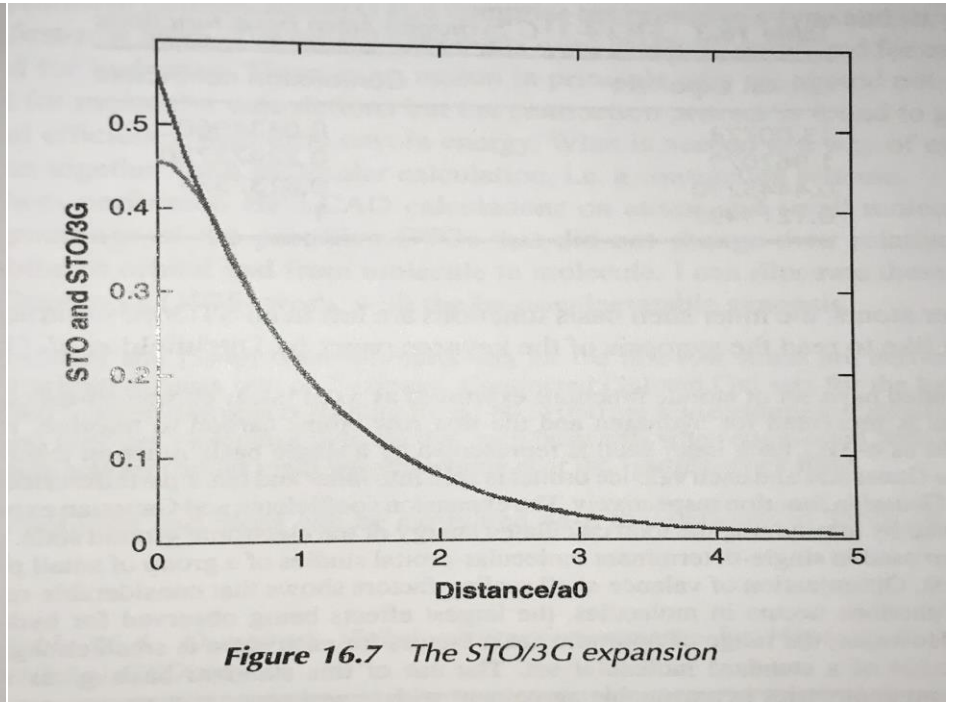
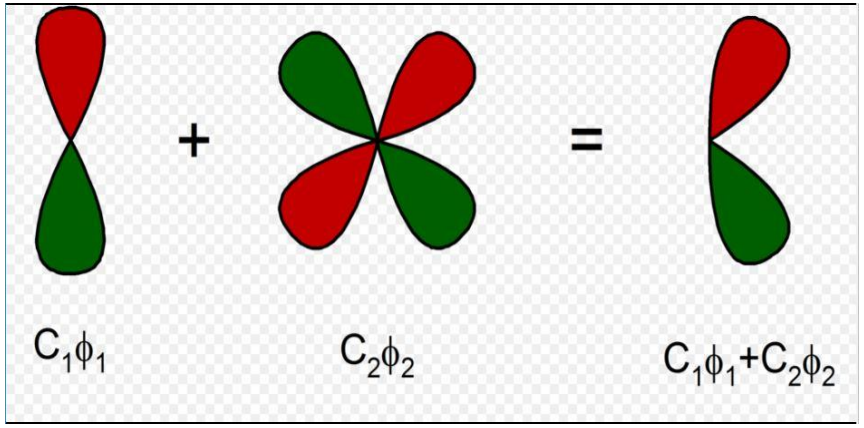


Figure 16.7 *The STO/3G expansion*

Credit: *Molecular Modelling for Beginners*, Alan Hinchliffe

Computational Chemistry

- Basis Sets
  - Sets of basis functions used to determine electron density in a molecule
  - Many sets exist, varying in size and complexity (and thus computational cost)
  - Example basis sets:
    - STO-nG: Minimal basis set, represents each AO as an STO approximated by *n* Gaussians
    - X-YZG: Pople basis sets, “split-valence”, represents each inner/non-valence AO with 1 STO approximated by X Gaussians, represents each valence AO with 2 STOs approximated by Y and Z Gaussians respectively
  - Basis sets may also contain:
    - Diffuse functions: Provide more flexibility for “tail” of atomic orbital (far from nucleus)
    - Polarization functions: Unoccupied *d* orbitals are included to better represent polarization of atoms



D polarization function added to P orbital

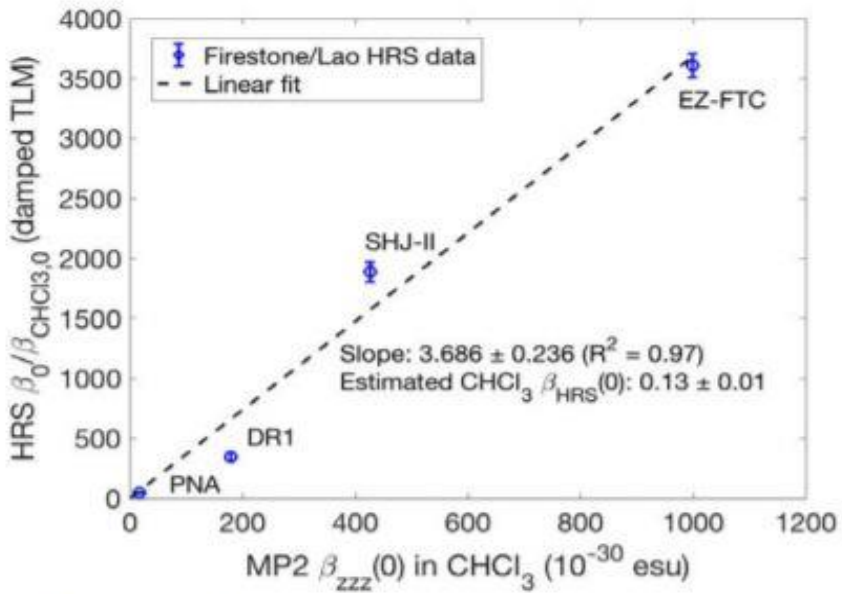
Computational Chemistry

- Methods in Computational Chemistry
  - HF: Hartree-Fock
    - Does not account for specific electron-electron repulsions (electron correlation), instead relies on an average field of electron correlation
    - Many-electron wavefunction takes form of a determinant of a matrix of single-electron wavefunctions (Slater Determinant)
  - DFT: Density Functional Theory
    - Energy as a functional of electron density. An exact functional is theorized to exist, but is currently unknown
    - Functionals used in my work: B3LYP, CAM-B3LYP, M062X, WB97X
  - MPn: Møller-Plesset Theory
    - Similar to HF, but specifically accounts for *n*th order electron correlations
    - MP2 is better than DFT, but ~1 order of magnitude more expensive
    - MP2 is occasionally used in my work

Can we do better with MP2?

- Hybrid DFT can do well for relative hyperpolarizabilities, but structure remains concern
- MP2 tractable on academic systems – appears nearly quantitative using Shelton $CHCl_3$ β_{HRS} of 0.16
- Still substantial scatter – would like to try CCSD or CCSD(T) and larger basis
- YLD-124 BLA: **0.06** (nearly identical to M062X), MBLD **0.02** (much less…)

Correlation between MP2 and HRS data



Damped TLM – fit dispersion as Lorentzian with 0.1 eV linewidth

Calculations: MP2/aug-cc-pVDZ//MP2/cc-pVDZ

Kimberly Firestone, *Frequency-agile hyper-Rayleigh scattering studies of nonlinear optical chromophores*, Ph.D thesis, University of Washington, **2004**

Slide taken from Johnson/Robinson presentation

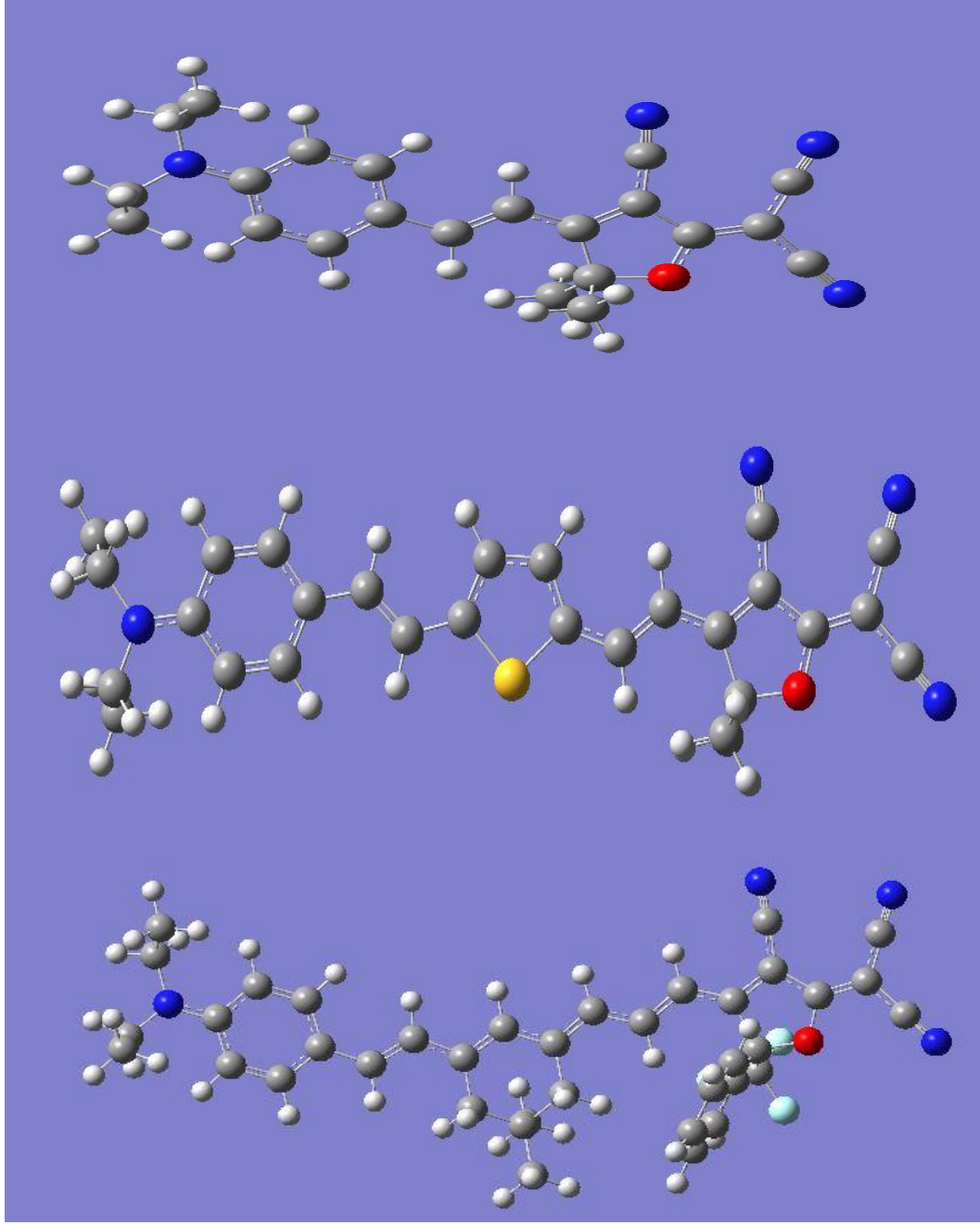
Quantitative Structure-Property Relationship (QSPR)

- QSPR models relate predictor variables (i.e. structure of a molecule, presence of functional groups/moieties) to a change in the magnitude of a chemical property
- Examples of predictors
  - Length of the conjugated backbone of a chromophore
  - Donor and acceptor used
- Examples of responses
  - Hyperpolarizability
  - Dipole moment

Initial Dataset

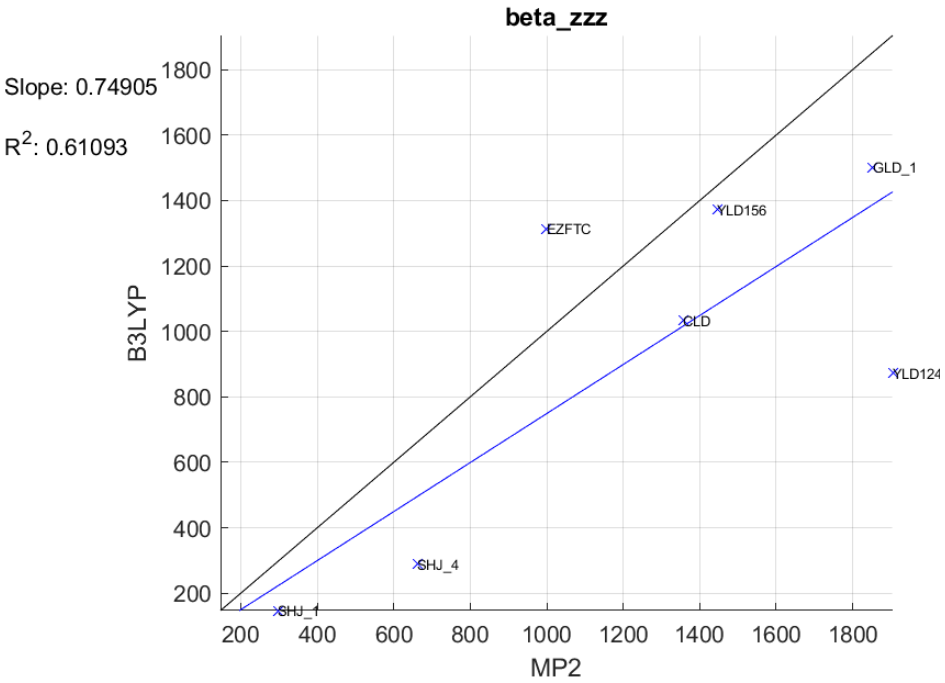
Initial Dataset - Overview

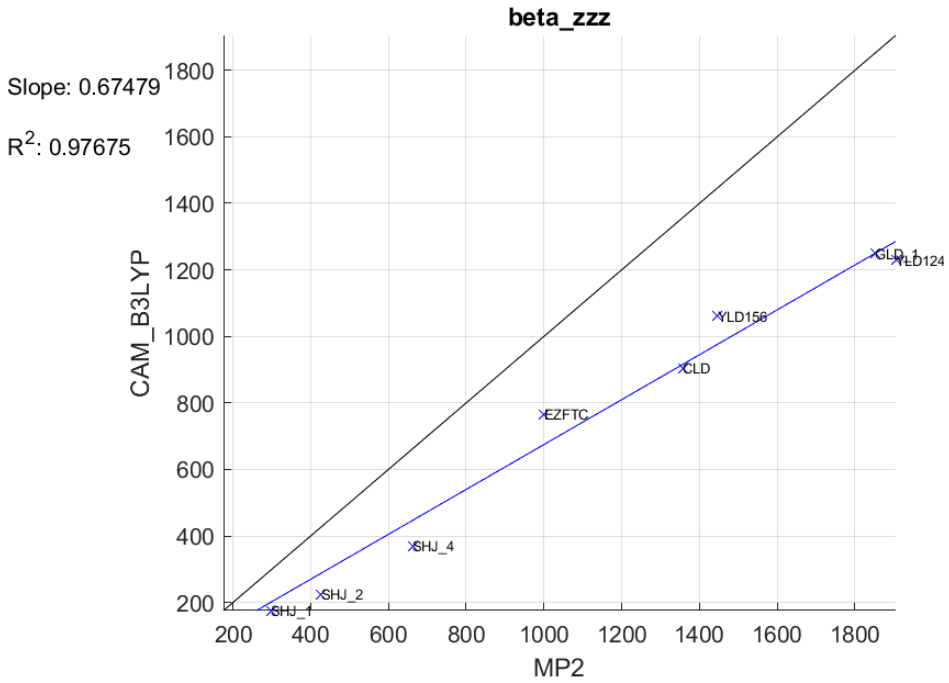
- Set of 26 molecules
- Primarily legacy chromophores
- Variety in sizes, structures, properties
  - Chain lengths range from 2 to 12 carbons
  - Some diversity in donor/acceptor groups
- Primarily used to compare different computational methods

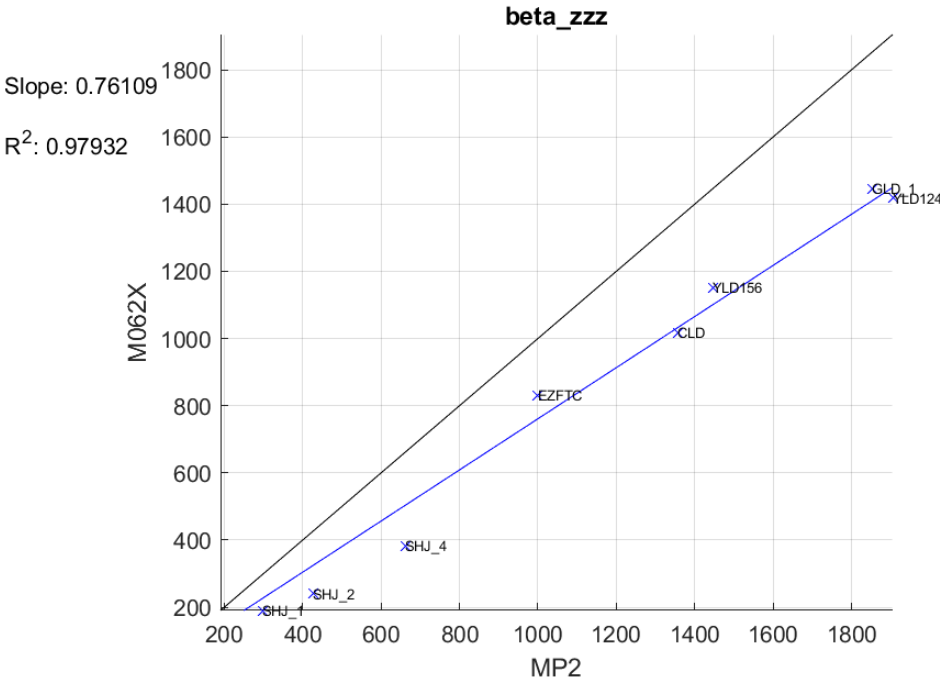


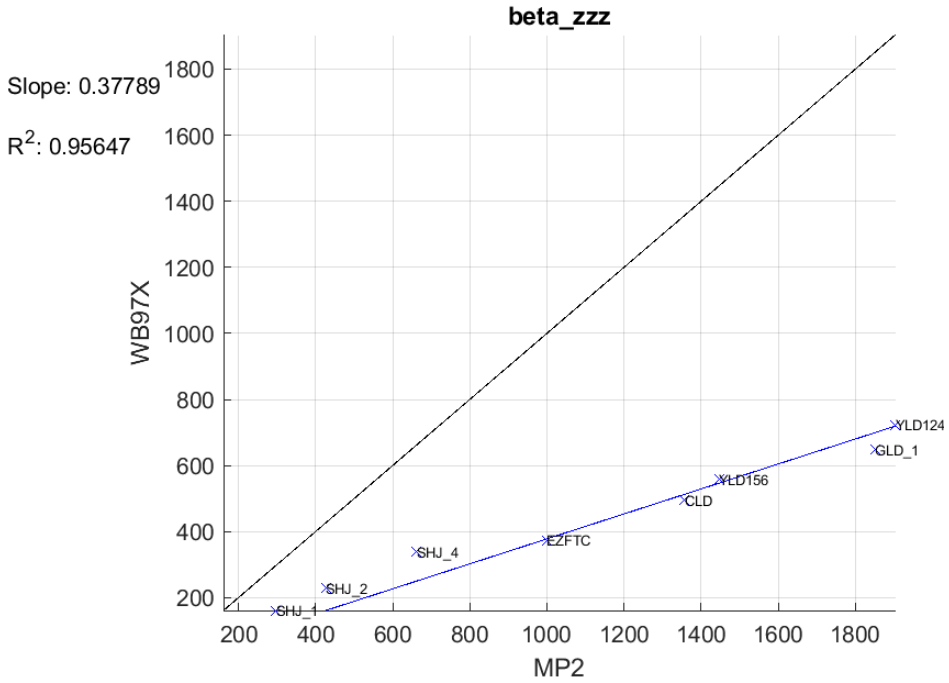
Example molecules from set. SHJ1, EZFTC, YLD124

Data









Example: Comparing hyperpolarizability values for DFT methods against MP2

A slope of 1 represents perfect agreement between methods. Y=x is plotted in black for reference

Initial Dataset – Method Property Comparisons

Correlations (R^2), larger is better

R^2 values for method comparison plots

All regressions have fixed y=0 intercept

Legend
R^2 > .85
.5 < R^2 < .85
R^2 < .5

Joe Hesse-Withbroe 7/24/2019

Alpha_iso

Method	B3LYP	CAM-B3LY	M062X	WB97X	MP2
B3LYP	---	0.867	0.767	0.885	0.903
CAM-B3LY	---	---	0.994	0.877	0.993
M062X	---	---	---	0.901	0.993
WB97X	---	---	---	---	0.991
MP2	---	---	---	---	---

Beta_hrs

Method	B3LYP	CAM-B3LY	M062X	WB97X	MP2
B3LYP	---	0.419	0.426	0.422	0.723
CAM-B3LY	---	---	0.995	0.905	0.988
M062X	---	---	---	0.908	0.98
WB97X	---	---	---	---	0.952
MP2	---	---	---	---	---

Mu_z

Method	B3LYP	CAM-B3LY	M062X	WB97X	MP2
B3LYP	---	0.728	0.726	0.378	0.637
CAM-B3LY	---	---	0.97	0.565	0.853
M062X	---	---	---	0.577	0.874
WB97X	---	---	---	---	0.969
MP2	---	---	---	---	---

Alpha_zz

Method	B3LYP	CAM-B3LY	M062X	WB97X	MP2
B3LYP	---	0.809	0.738	0.799	0.475
CAM-B3LY	---	---	0.917	0.825	0.443
M062X	---	---	---	0.822	0.566
WB97X	---	---	---	---	0.38
MP2	---	---	---	---	---

Beta_zzz

Method	B3LYP	CAM-B3LY	M062X	WB97X	MP2
B3LYP	---	0.372	0.369	0.363	0.619
CAM-B3LY	---	---	0.989	0.877	0.977
M062X	---	---	---	0.884	0.979
WB97X	---	---	---	---	0.956
MP2	---	---	---	---	---

Lambda_max

Method	B3LYP	CAM-B3LY	M062X	WB97X	MP2
B3LYP	---	0.829	0.841	0.611	---
CAM-B3LY	---	---	0.995	0.763	---
M062X	---	---	---	0.743	---
WB97X	---	---	---	---	---
MP2	---	---	---	---	---

Alpha Ratio

Method	B3LYP	CAM-B3LY	M062X	WB97X	MP2
B3LYP	---	0.703	0.749	0.652	0.601
CAM-B3LY	---	---	0.988	0.712	0.952
M062X	---	---	---	0.709	0.952
WB97X	---	---	---	---	0.824
MP2	---	---	---	---	---

Beta Ratio

Method	B3LYP	CAM-B3LY	M062X	WB97X	MP2
B3LYP	---	0.49	0.489	0.477	0.099
CAM-B3LY	---	---	0.89	0.721	0.34
M062X	---	---	---	0.722	0.515
WB97X	---	---	---	---	0.642
MP2	---	---	---	---	---

Initial Dataset – Method Property Comparisons

Agreements (Slope), closer to 1 is better

Slopes for method comparison plots

All regressions have fixed y=0 intercept

Legend

.85 < Slope < 1.176	
.5 < Slope < .85	1.176 < Slope < 2
Slope < .5	2 < Slope

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Alpha_iso

Method	B3LYP	CAM-B3LY	M062X	WB97X	MP2
B3LYP	---	0.769	0.768	0.598	1.245
CAM-B3LY	---	---	0.993	0.773	0.944
M062X	---	---	---	0.778	0.942
WB97X	---	---	---	---	0.792
MP2	---	---	---	---	---

Beta_hrs

Method	B3LYP	CAM-B3LY	M062X	WB97X	MP2
B3LYP	---	0.954	1.066	0.472	0.852
CAM-B3LY	---	---	1.106	0.49	0.732
M062X	---	---	---	0.443	0.8
WB97X	---	---	---	---	0.407
MP2	---	---	---	---	---

Mu_z

Method	B3LYP	CAM-B3LY	M062X	WB97X	MP2
B3LYP	---	0.756	0.7285	0.612	1.548
CAM-B3LY	---	---	0.959	0.817	1.231
M062X	---	---	---	0.851	1.192
WB97X	---	---	---	---	1.078
MP2	---	---	---	---	---

Alpha_zz

Method	B3LYP	CAM-B3LY	M062X	WB97X	MP2
B3LYP	---	0.694	0.738	0.49	1.119
CAM-B3LY	---	---	1.019	0.686	0.722
M062X	---	---	---	0.664	0.764
WB97X	---	---	---	---	0.546
MP2	---	---	---	---	---

Beta_zzz

Method	B3LYP	CAM-B3LY	M062X	WB97X	MP2
B3LYP	---	0.959	1.115	0.486	0.749
CAM-B3LY	---	---	1.14	0.503	0.675
M062X	---	---	---	0.441	0.761
WB97X	---	---	---	---	0.378
MP2	---	---	---	---	---

Lambda_max

Method	B3LYP	CAM-B3LY	M062X	WB97X	MP2
B3LYP	---	0.833	0.848	0.702	---
CAM-B3LY	---	---	1.011	0.849	---
M062X	---	---	---	0.837	---
WB97X	---	---	---	---	---
MP2	---	---	---	---	---

Alpha Ratio

Method	B3LYP	CAM-B3LY	M062X	WB97X	MP2
B3LYP	---	0.931	0.934	0.845	1.087
CAM-B3LY	---	---	1.001	0.908	1.006
M062X	---	---	---	0.906	1.008
WB97X	---	---	---	---	0.94
MP2	---	---	---	---	---

Beta Ratio

Method	B3LYP	CAM-B3LY	M062X	WB97X	MP2
B3LYP	---	0.449	0.431	0.436	1.121
CAM-B3LY	---	---	0.973	0.995	1.074
M062X	---	---	---	1.022	1.047
WB97X	---	---	---	---	1.072
MP2	---	---	---	---	---

Initial Dataset – Method Property Comparisons

- Findings:
  - Weak agreement between DFT functionals and MP2
    - Systematic differences in calculations --- weak agreement expected, not concerning
  - All methods except B3LYP correlate well with each other for *properties*
    - Helpful --- weak agreements can be reliably corrected if correlations are strong
  - Weaker correlations between methods for alpha & beta *ratios*
    - More deviation between methods in the minor components of (hyper)polarizabilities

Initial Dataset – Method Structure Comparisons

Correlation (R^2)

BLA

Method	B3LYP	CAM-B3LY	M062X	WB97X	MP2
B3LYP	---	0.563	0.575	0.463	0.542
CAM-B3LY	---	---	0.978	0.83	0.449
M062X	---	---	---	0.829	0.494
WB97X	---	---	---	---	0.441
MP2	---	---	---	---	---

BOA

Method	B3LYP	CAM-B3LY	M062X	WB97X	MP2
B3LYP	---	0.696	0.523	0.673	0.025
CAM-B3LY	---	---	0.54	0.995	0.024
M062X	---	---	---	0.045	0.948
WB97X	---	---	---	---	0.025
MP2	---	---	---	---	---

MBLD

Method	B3LYP	CAM-B3LY	M062X	WB97X	MP2
B3LYP	---	0.925	0.834	0.858	
CAM-B3LY	---	---	0.933	0.948	
M062X	---	---	---	0.971	
WB97X	---	---	---	---	
MP2	---	---	---	---	---

Agreement (Slope)

BLA

Method	B3LYP	CAM-B3LY	M062X	WB97X	MP2
B3LYP	---	2.028	1.918	2.688	0.531
CAM-B3LY	---	---	1.017	1.364	0.9
M062X	---	---	---	1.365	0.93
WB97X	---	---	---	---	1.193
MP2	---	---	---	---	---

BOA

Method	B3LYP	CAM-B3LY	M062X	WB97X	MP2
B3LYP	---	1.136	1.379	1.207	0.721
CAM-B3LY	---	---	1.206	1.065	0.775
M062X	---	---	---	0.828	0.993
WB97X	---	---	---	---	0.817
MP2	---	---	---	---	---

MBLD

Method	B3LYP	CAM-B3LY	M062X	WB97X	MP2
B3LYP	---	1.067	1.002	0.962	
CAM-B3LY	---	---	0.922	0.878	
M062X	---	---	---	0.955	
WB97X	---	---	---	---	
MP2	---	---	---	---	---

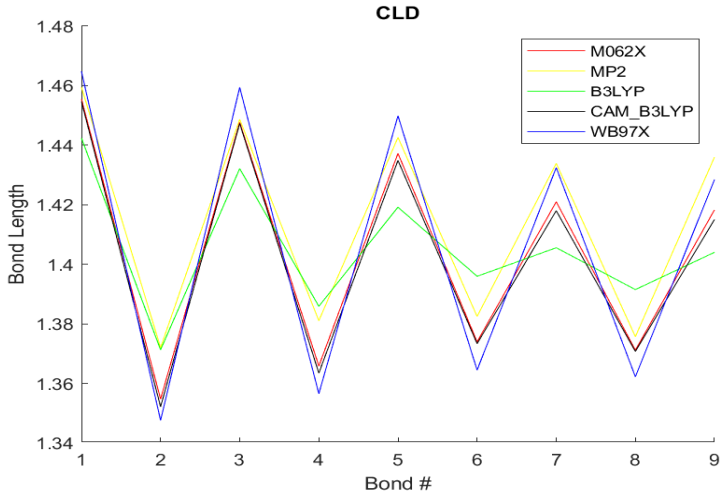
BLA: Difference between average double bond length and average single bond length (Geometric property)

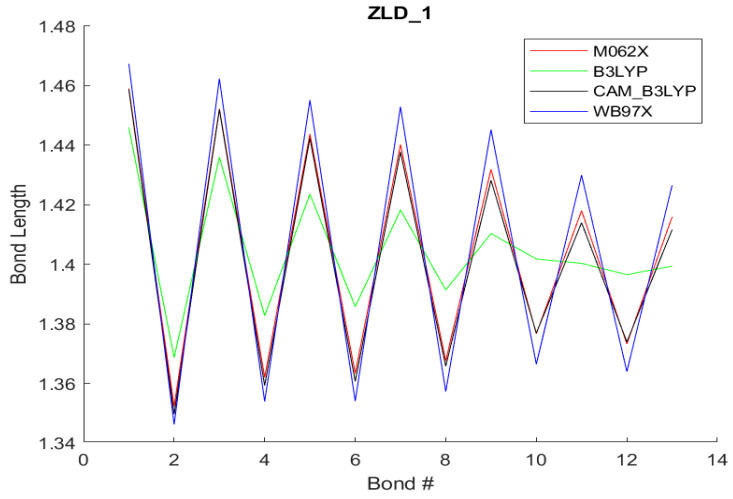
BOA: Difference between average double bond order and average single bond order (Electronic property)

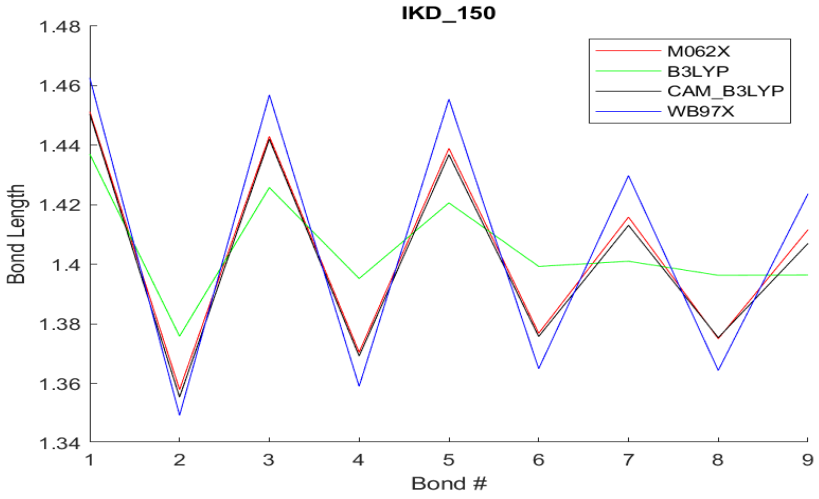
MBLD: Measure of change in chain conjugation along a molecule's backbone (Geometric property)

Initial Dataset – Method Structure Comparisons

- Findings:
  - Weak correlation & agreement between methods for BLA, yet strong correlation & agreement for MBLD
  - Weak correlation & agreement between methods for BOA
    - Electronic properties have greater variation by method than geometric properties







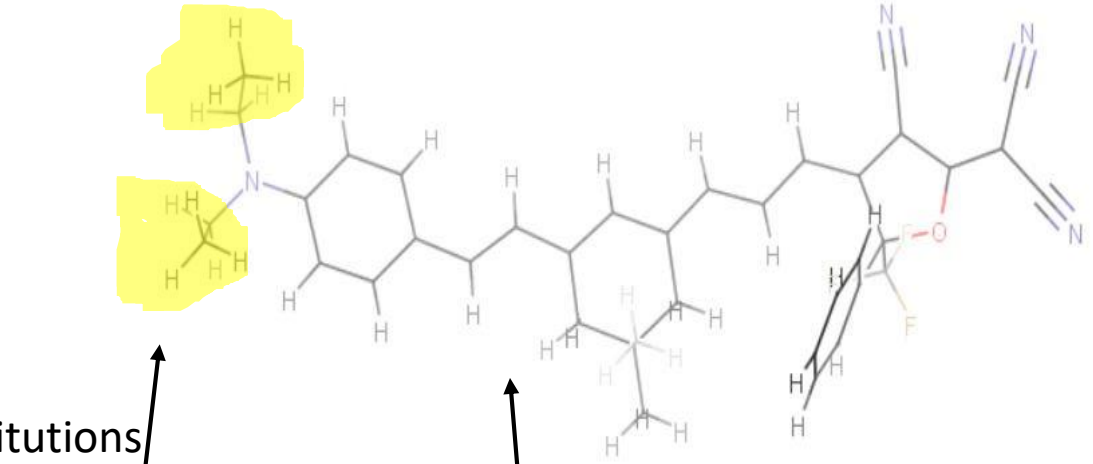
Other Studies & Sets

Most still in progress

YLD-124 Variants Set

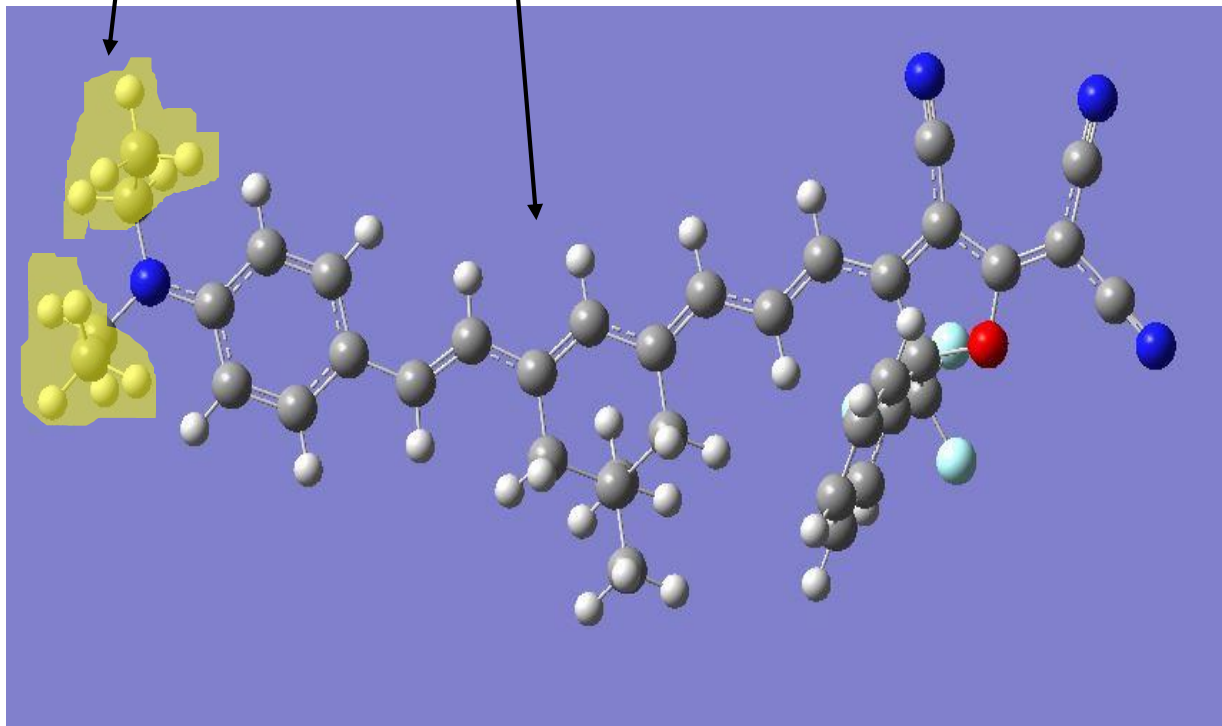
YLD Variants - Overview

- All have identical backbone
- R1 and R2 are substituted
- 21 molecules

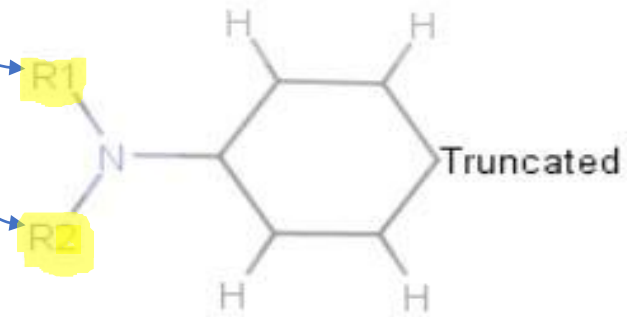


Substitutions made

Common to all Molecules in group



Substitute various R groups,
Compare parameters/properties
(Hammett, BLA/BOA, etc)



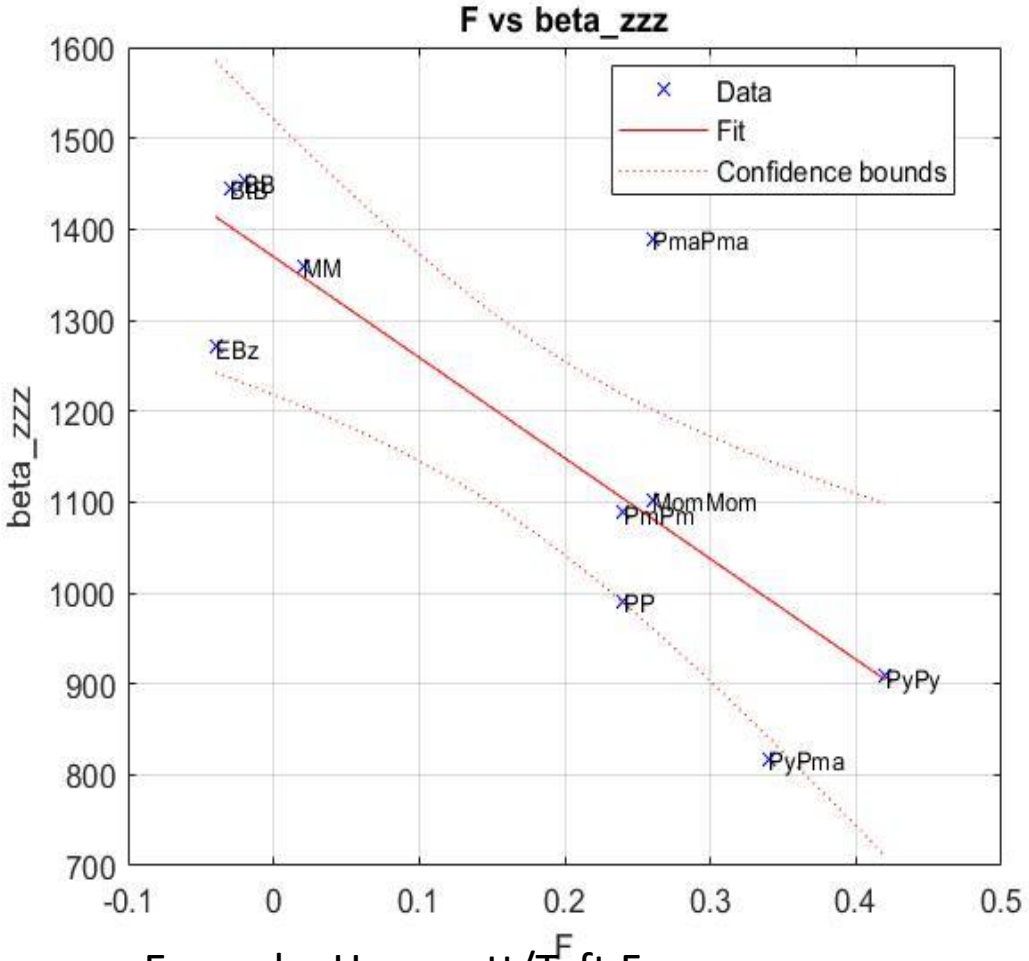
YLD124 - Studies

- Hammett Parameters & Molecular Properties Correlation
  - Comparison between Hammett parameters of donor groups and molecular properties

Slope:
-1107.3207

Y-int:
1369.611

R^2:
0.65934



Example: Hammett/Taft F parameter vs beta

YLD124 Variants – Hammett Parameters vs Molecular Properties

- More validation needed. Two outliers significantly skewed results
- Weak to no correlation including two outliers

SigP	Mu_z	betaZZZ	Lambda
Correlatio	0.0734	0.0078	0.00757

F	Mu_z	betaZZZ	Lambda
Correlatio	0.247	0.289	0.236

SigM	Mu_z	betaZZZ	Lambda
Correlatio	0.228	0.172	0.143

R	Mu_z	betaZZZ	Lambda
Correlatio	~0	0.0488	0.037

- Much stronger correlations excluding outliers

SigP	Mu_z	betaZZZ	Lambda
Correlatio	0.289	0.675	0.483

F	Mu_z	betaZZZ	Lambda
Correlatio	0.479	0.659	0.653

SigM	Mu_z	betaZZZ	Lambda
Correlatio	0.4128	0.721	0.615

R	Mu_z	betaZZZ	Lambda
Correlatio	0.12	0.477	0.254

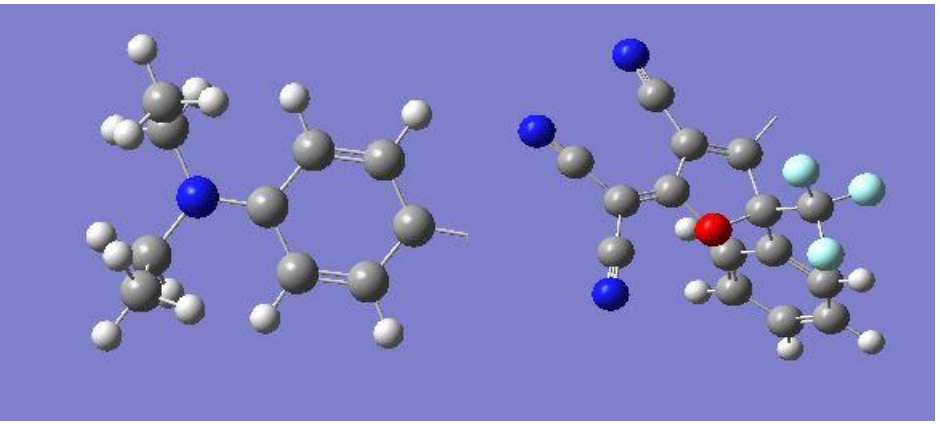
Thanks!

Chain Length Dataset

(Everything here was backup for final presentation 7/25/2019, but was ultimately not presented on)

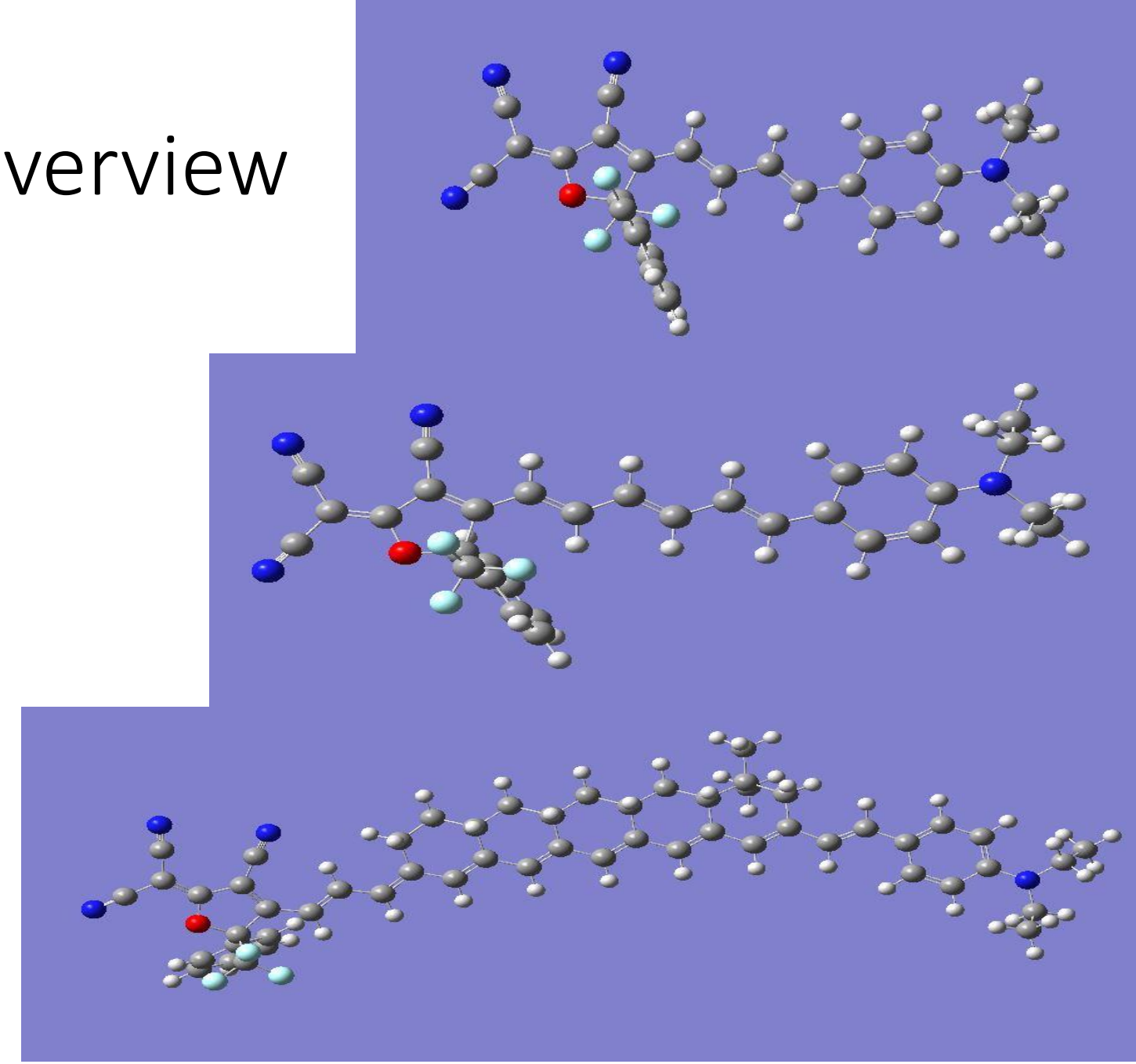
Lengths Dataset - Overview

- Set of 8 molecules
- Donor/Acceptor Constant
- Chain size varied



Donor

Acceptor



Example molecules from set. ALD1, BLD1, QLD1

Lengths Dataset – Studies

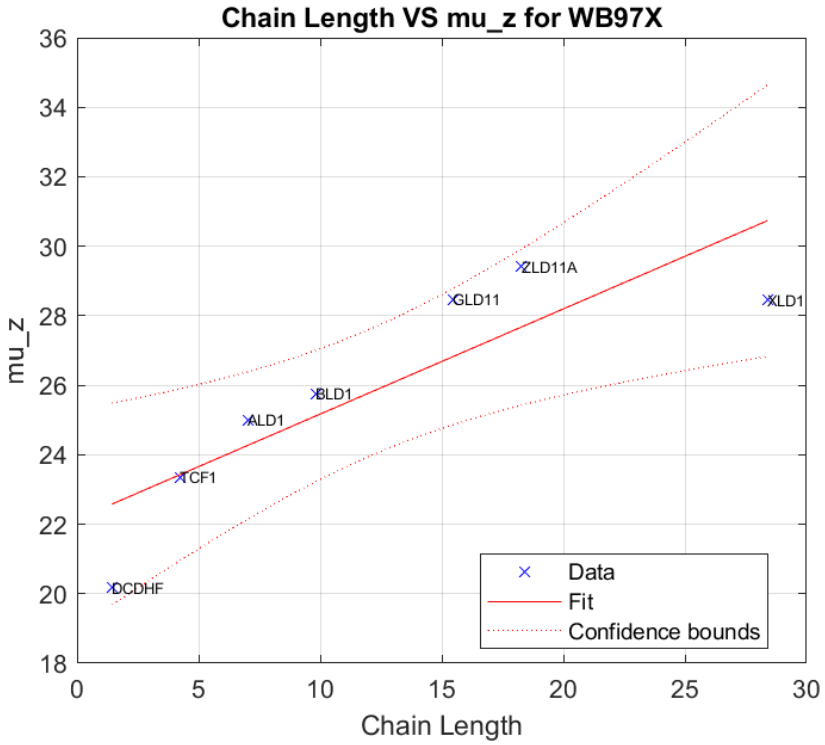
- Molecule Properties vs Length

	Mu_z	alpha_iso	alpha_zz	alphaRatio	betaHRS	betaZZZ	betaRatio
Correlatio	0.729	0.948	0.121	0.0176	0.959	0.967	0.442
Slope	0.303	5.227	2.858	1.672	24.502	53.282	-0.00326
Intercept	22.145	66.793	125.082	0.652	39.801	63.78	0.534

Slope:
0.30263

Y-int:
22.1447

R^2:
0.72966



Example: Examining dipole moment as a function of chain length

Lengths Dataset – Properties vs Length

- Similar diminishments with increasing length