Size-Dependence of Percent Hartree-Fock Exchange in Hybrid DFT Functionals

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Pomona College Intensive Summer Experience Symposium

Acknowledgments

- Co-Collaborators:
  - Dr. Lewis Johnson (University of Washington)
  - Dr. Bruce Robinson (University of Washington)
- Other Thanks:
  - Dalton/Robinson Lab (University of Washington)
  - Dr. Gordon Stecklein (Pomona College & Efficient Power Conversion) – RAISE Project Advisor
  - Dr. Malkiat Johal (Pomona College)
- Institutional:
  - Pomona College – 2020 RAISE Program
    - The R. Nelson Smith ‘38 and Corwin H. Hansch Fund
  - University of Washington – Computing Resources
    - Student Technology Fund

Background

Outline

BACKGROUND

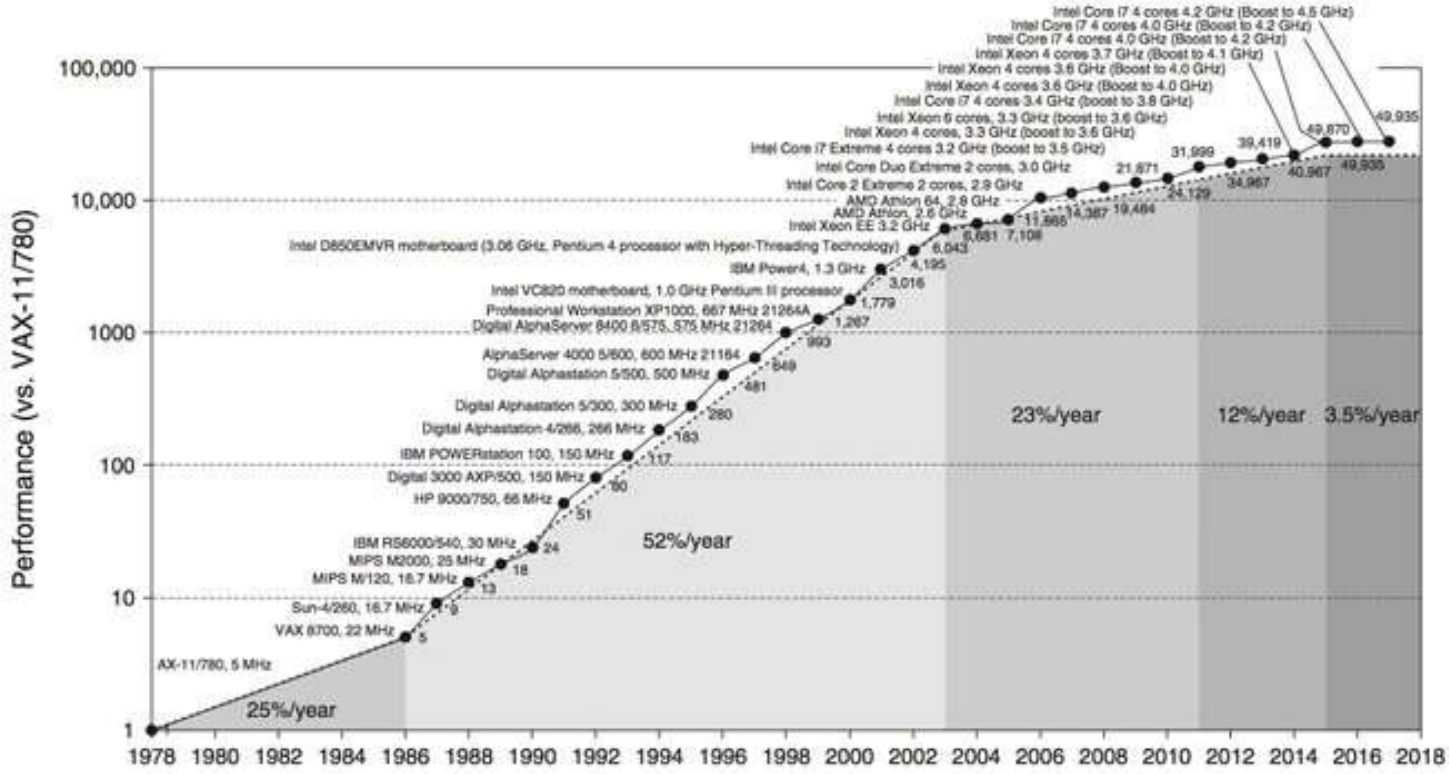
Methods

Results

Conclusions

Future Work

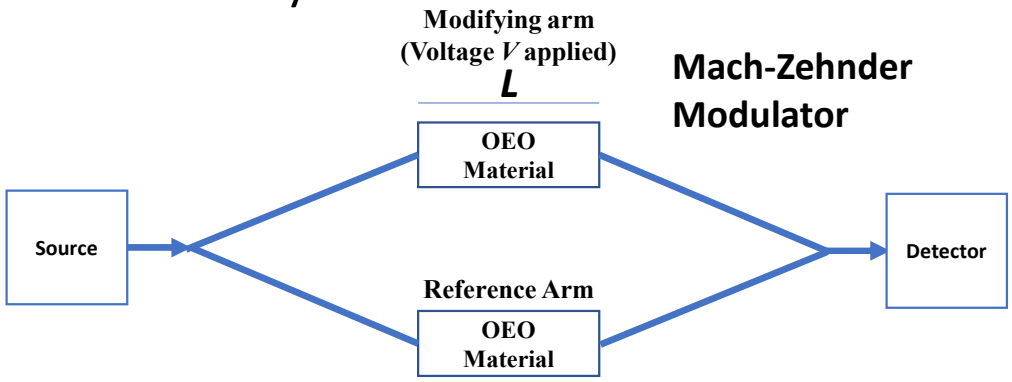
Background – Moore's Law



- Improvement in electronics performance stagnating
- Power costs climbing

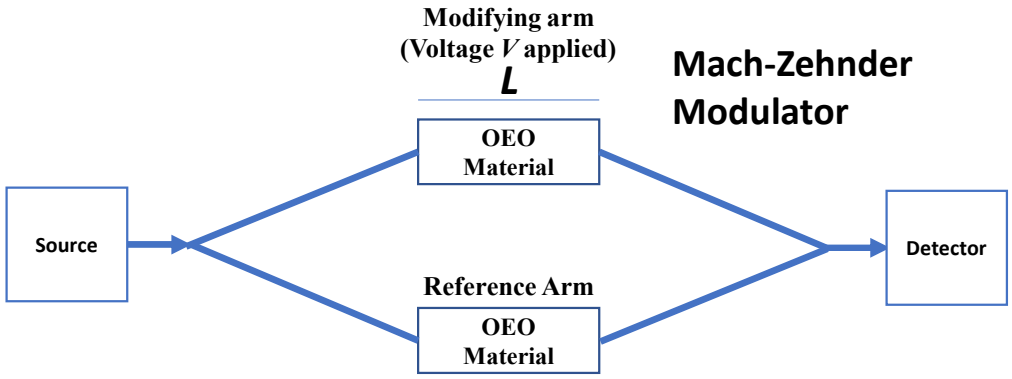
Background – Photonics

- Computing with photons, not electrons
- Encode binary information on light wave
  - Split light wave into two waveguides with OEO material
  - Selectively apply voltage to one waveguide – changes index of refraction n (Pockels Effect)
  - Recombine two waves
    - Voltage – 180° phase shift – binary 0
    - No voltage – 0° phase shift – binary 1



Background – Integrating electronics & photonics

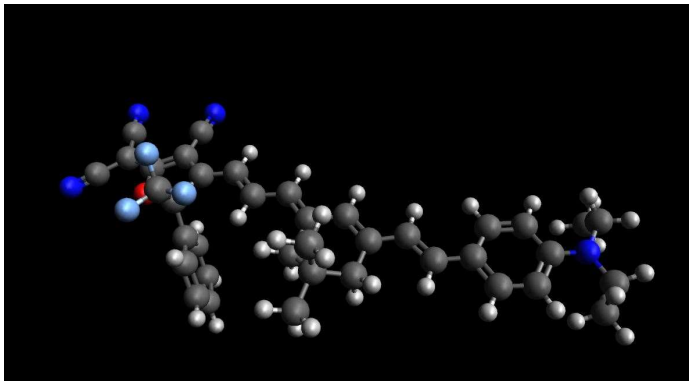
- Goal: Chip-scale modulators working at standard voltages
- $V_\pi L$: Voltage-length product -- length needed for a 180° phase shift in the period of the light at a given voltage
  - Minimize $V_\pi L$ -- Pockels effect: $\Delta n \propto N\beta\langle cos^3\theta\rangle$
    - Maximize Δn:
      - $\langle cos^3\theta\rangle$ – acentric ordering
      - N – chromophore density
      - β – chromophore hyperpolarizability



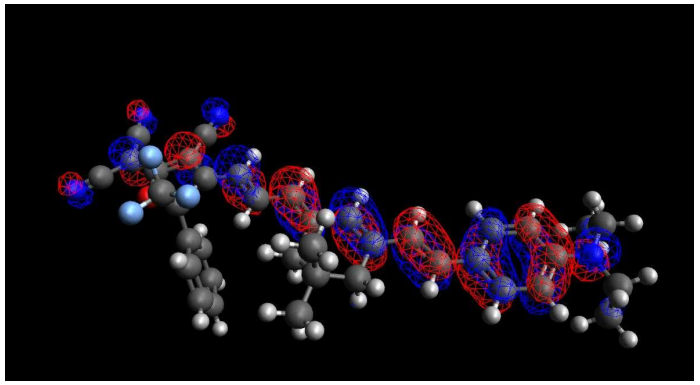
Background – Computational Chemistry

- Computational Chemistry:
  - Calculate approximate solutions to many-electron problems
  - Balance compute time with physical accuracy
  - Predict chromophore properties & effectiveness

Ex: Where do a molecule's electrons reside?



This electron is delocalized along the chain.

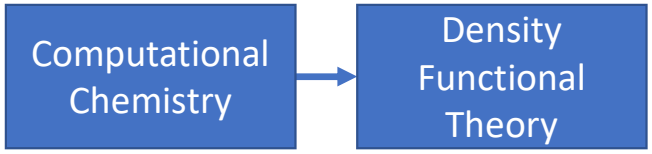


YLD124 HOMO calculated using M062X

Computational Chemistry

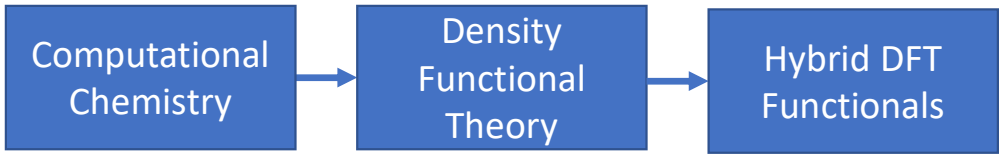
Background – Density Functional Theory

- Density Functional Theory (DFT):
  - Commonly used method in computational chemistry
  - Uses a functional (function of a function) of electron spatial density to calculate electronic structure
    - Many different functionals exist: B3LYP, M062X, etc.
  - Developed in the 70s, popular by the 90s following improvements in accounting for electron exchange & correlation effects



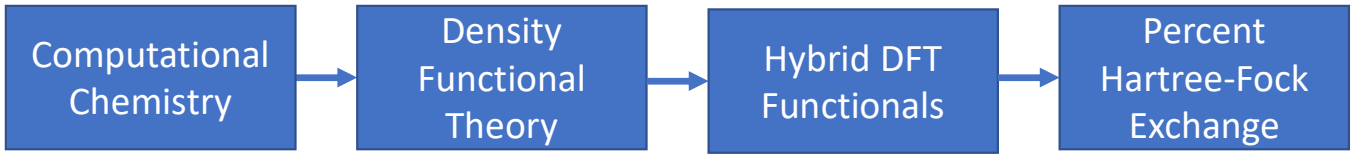
Background – Hybrid Functionals

- Hybrid Functionals:
  - Functionals must account for electron exchange and correlation
  - Hybrid functionals incorporate a certain percentage of exact Hartree-Fock exchange energy (%HFX)
  - Percentage of HFX varies
    - B3LYP – 20%
    - M062X – 54%
    - CAM-B3LYP – 20%-65% depending on distance



Background – Key Question

- Does the percentage of HFX needed to accurately model charge transfer systems depend on the size of molecule?

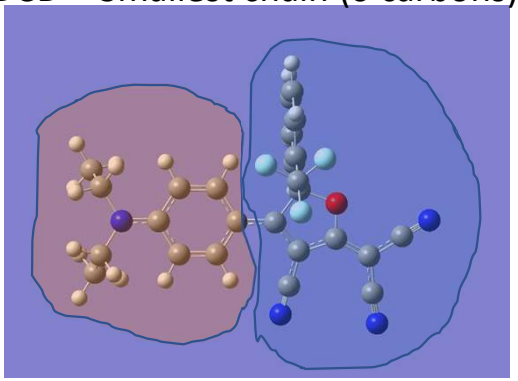


Methods

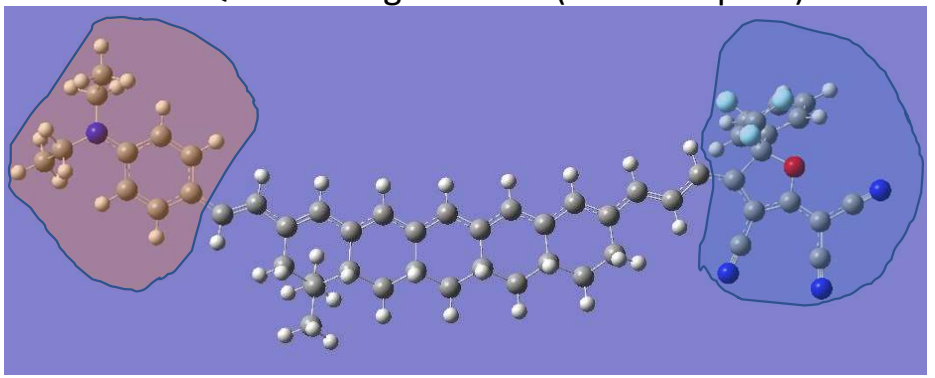
Methods – "Materials"

- Molecule set:
  - 9 molecules – organic electro-optic chromophores
  - Electron donor – conjugated bridge – electron acceptor
  - Same donor and acceptor, vary only in length of bridge
- Functional suite:
  - 9 functionals, mainly derivatives of B3LYP (20% HFX)
  - Vary in percentage of HF exchange

DCD – Smallest chain (0 carbons)



QLD1 – Longest chain (8 carbon pairs)



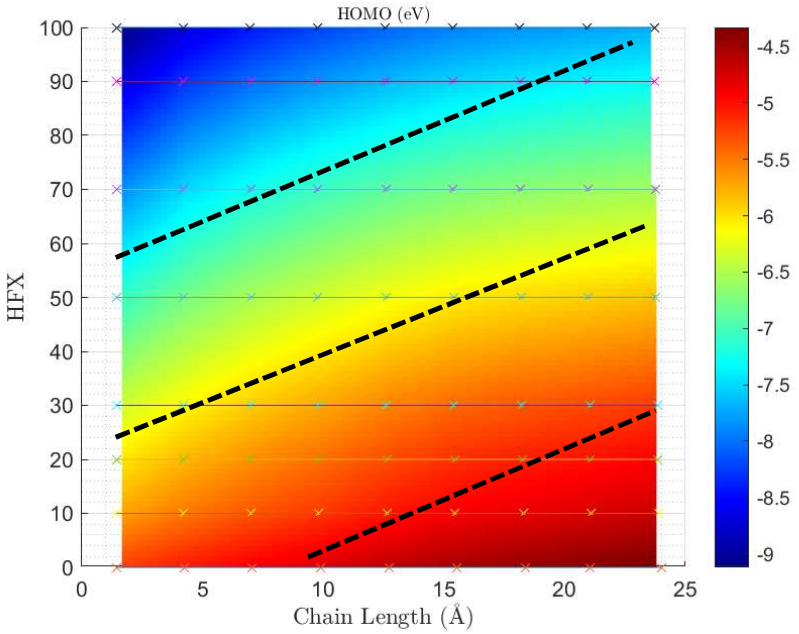
Methods – Experimental Methods

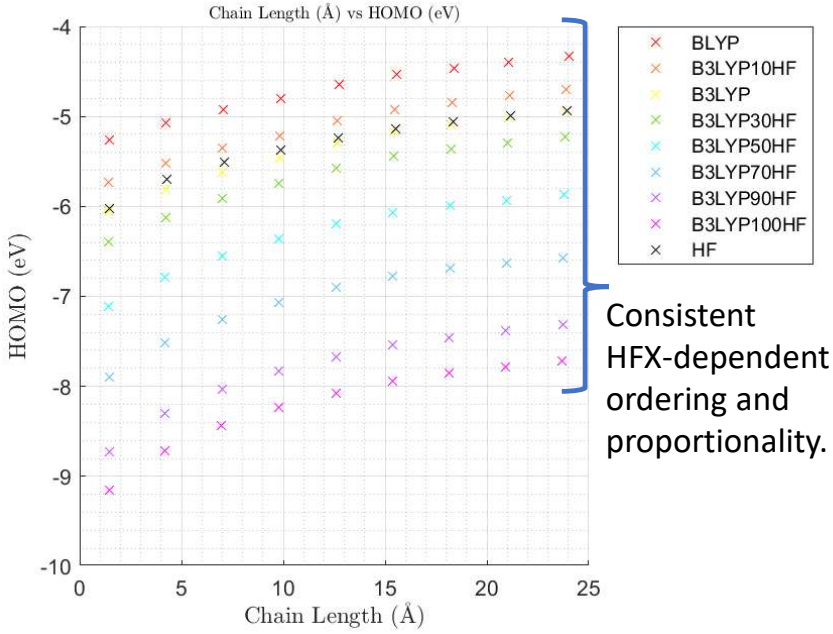
- Compute electronic structure (ground & first excited/CT state) for each of the 9 molecules using each of the 9 methods
- Plot molecular properties as function of chain length and HFX, search for deviations from linearity

Results

Results – Linear dependency for all %HFX

- Some properties exhibit an approximately-linear relationship to all levels of %HFX.





Consistent HFX-dependent ordering and proportionality.

HOMO linearly dependent on both chain length and HFX.
Appropriateness of linear approximation is independent of HFX and molecule size.

Outline

Background

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RESULTS

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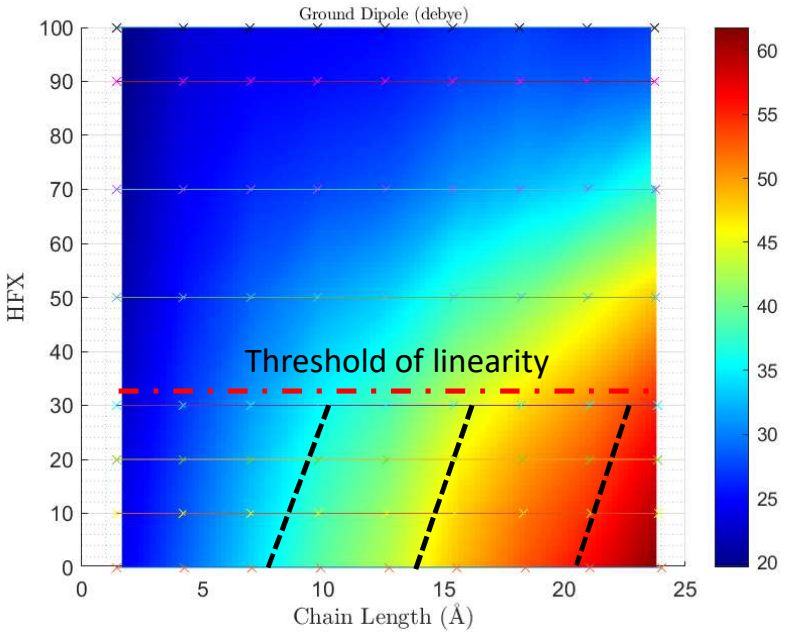
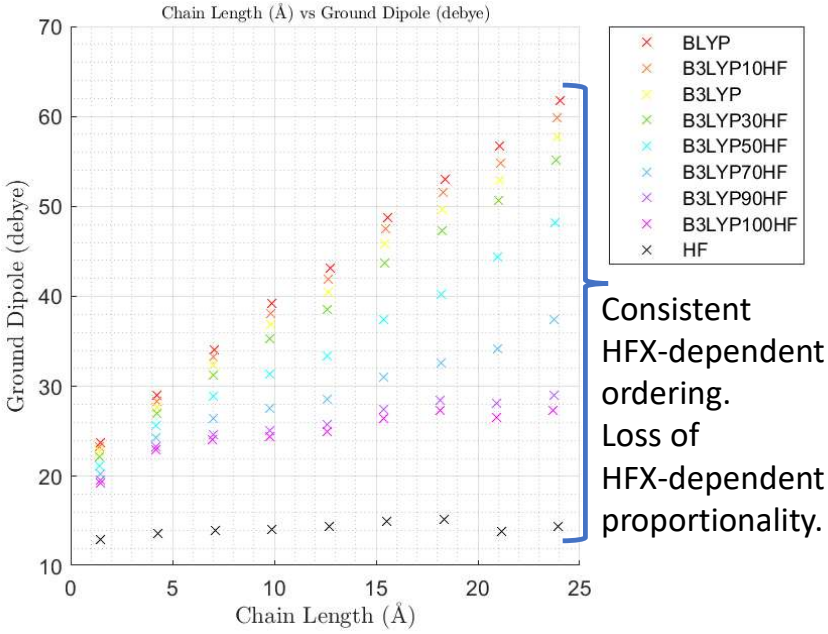
Future Work

Results – Linear dependency for low %HFX

- Some properties exhibit an approximately-linear relationship to low levels of %HFX only

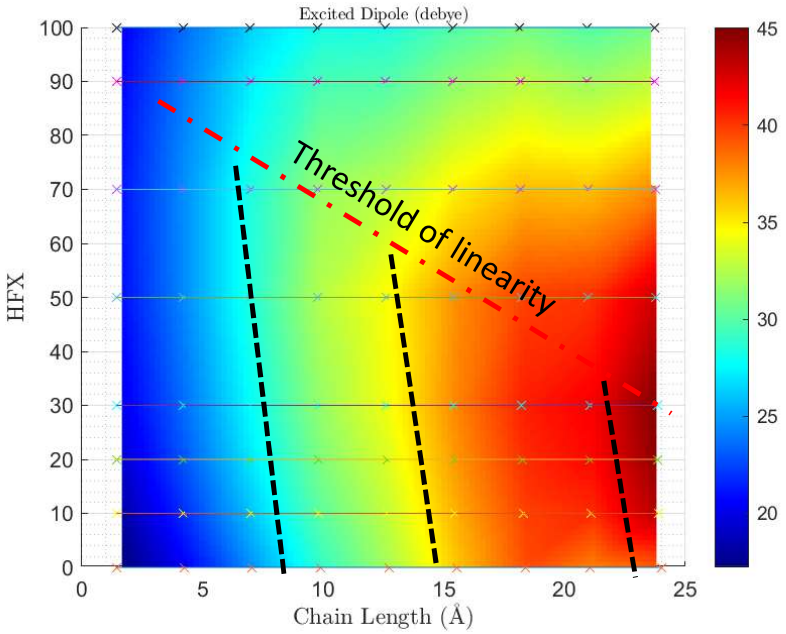


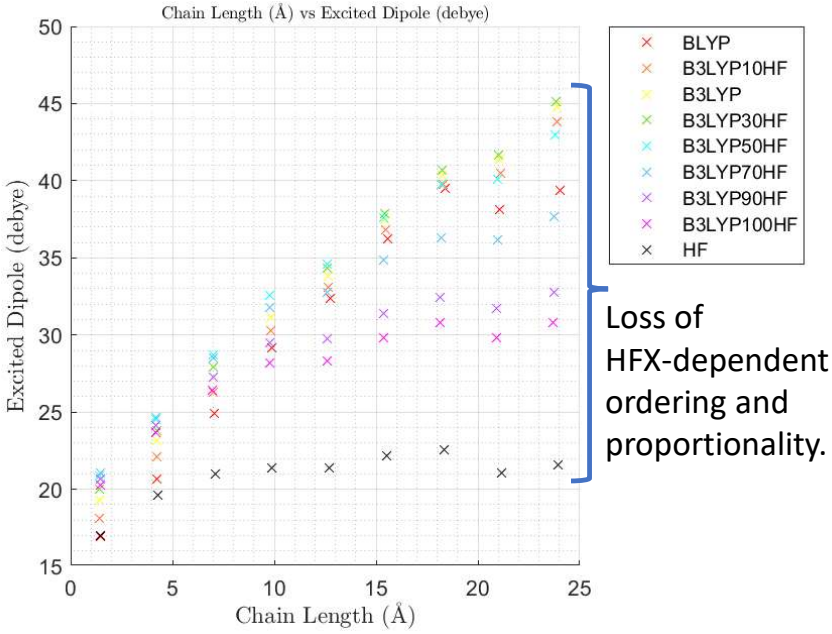


Ground dipole linearly dependent on chain length and HFX below a specific HFX.
Appropriateness of linear approximation depends on HFX.

Results – Nonlinear dependencies

- Key determinants of chromophore performance have more complex behaviors.

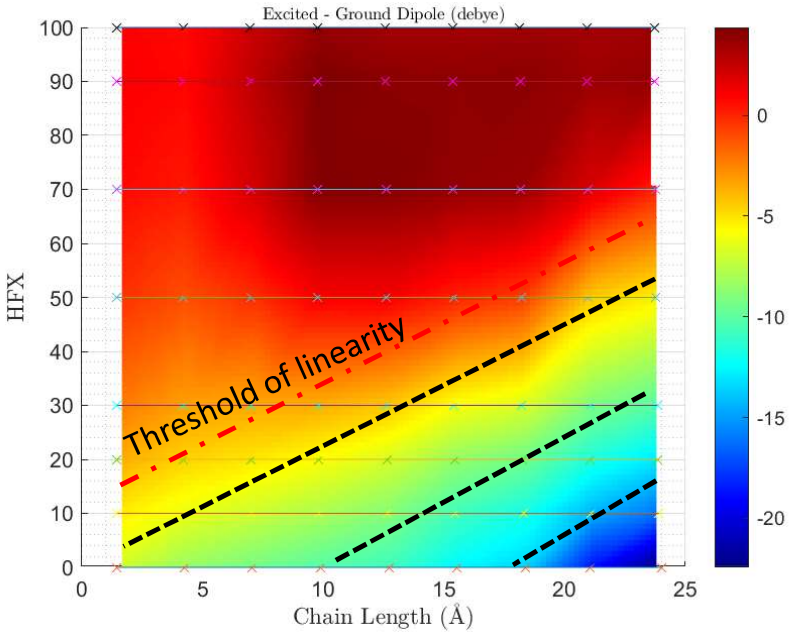


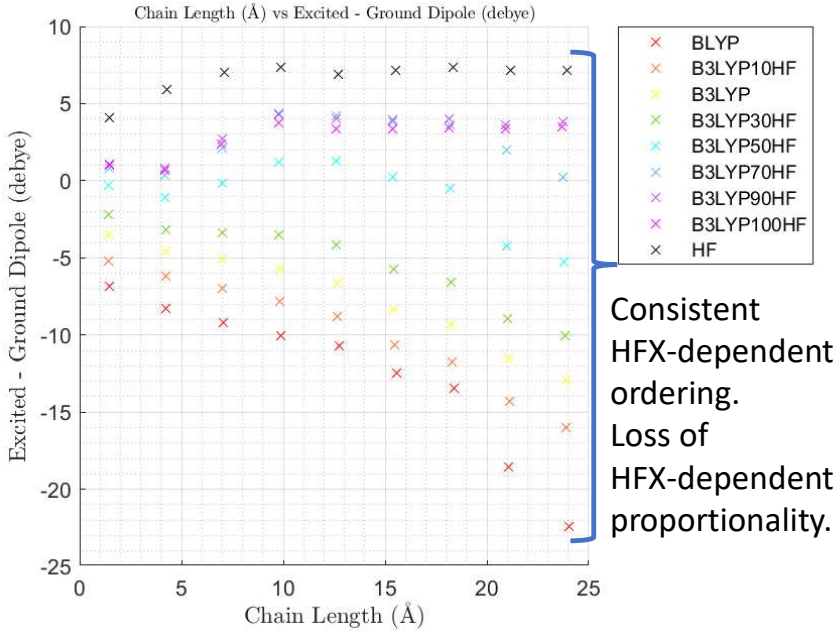


Appropriateness of linear approximation depends on both HFX and molecular size.
Above a certain chain length, linear approximation invalid regardless of HFX.

Results – Nonlinear dependencies

- Key determinants of chromophore performance have more complex behaviors.



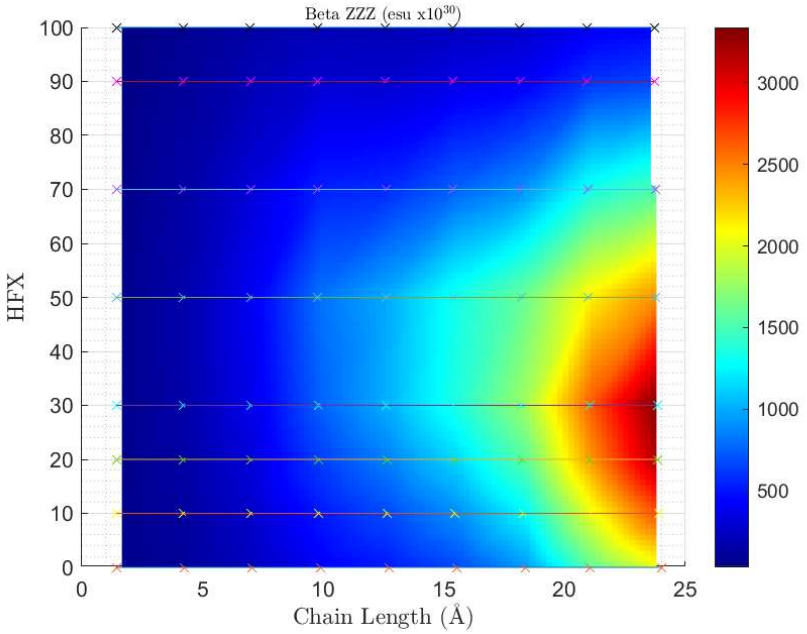


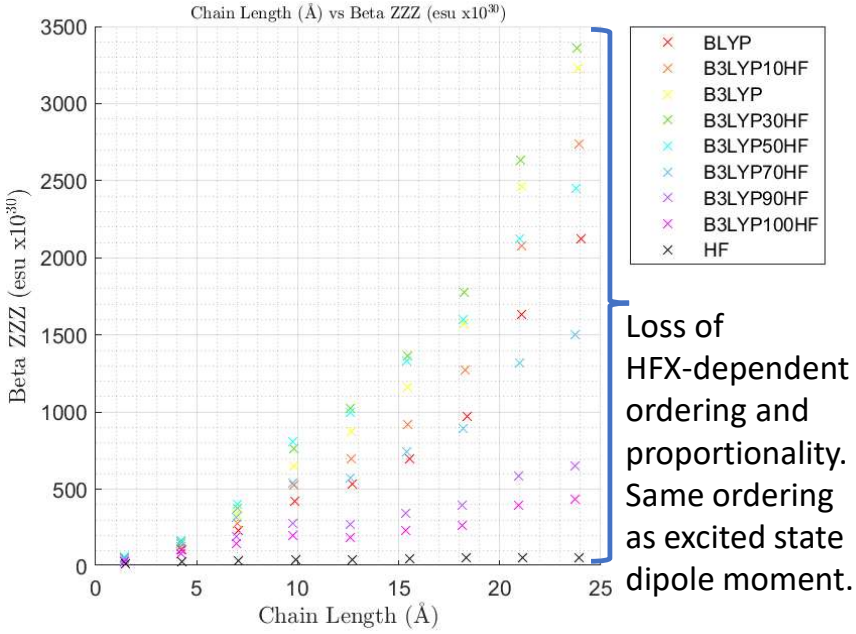
Consistent HFX-dependent ordering.
Loss of HFX-dependent proportionality.

Appropriateness of linear approximation depends on both HFX and molecular size.

Results – Nonlinear dependencies

- Key determinants of chromophore performance have more complex behaviors.





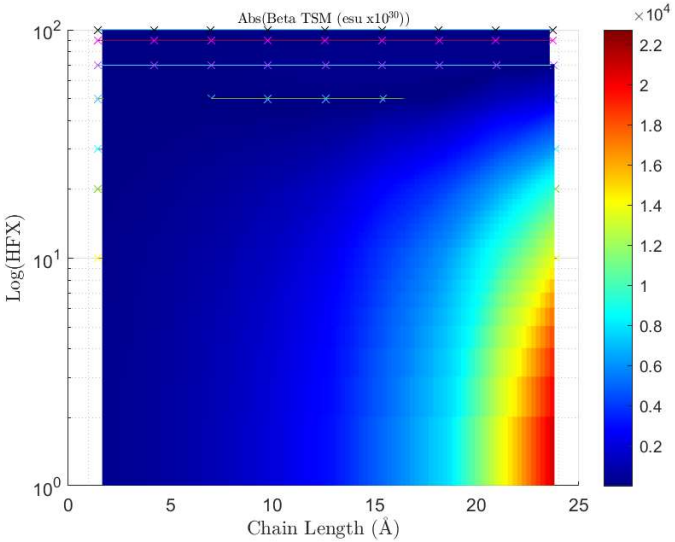
Loss of HFX-dependent ordering and proportionality. Same ordering as excited state dipole moment.

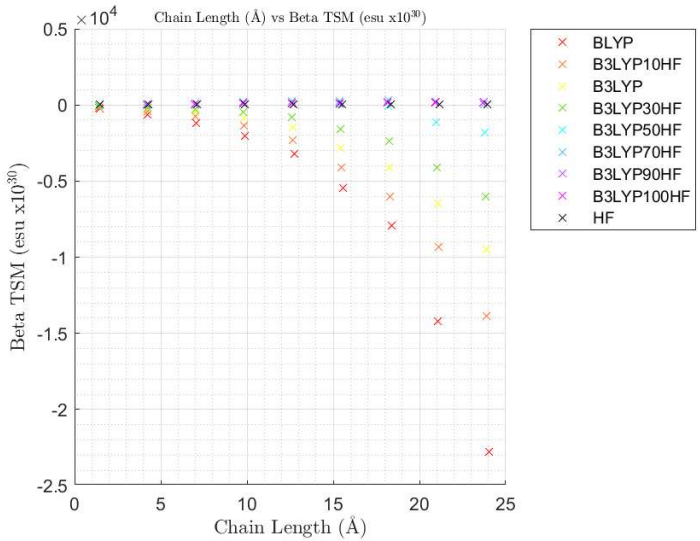
Linear approximation inappropriate regardless of molecular size and HFX.

Results – Two State Model

- Two State Model: Estimate of hyperpolarizability using excitation energy and ground, transition, and excited state dipole moments:

$$\beta_{TSM} = (\mu_e - \mu_g)\left(\frac{\mu_{trans}}{E_{trans}}\right)^2 \propto \beta_{zzz}$$



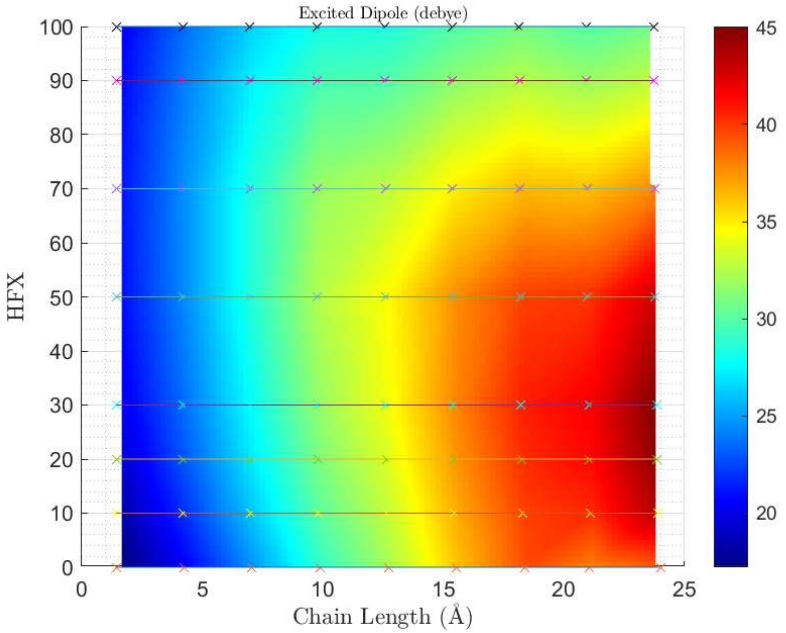


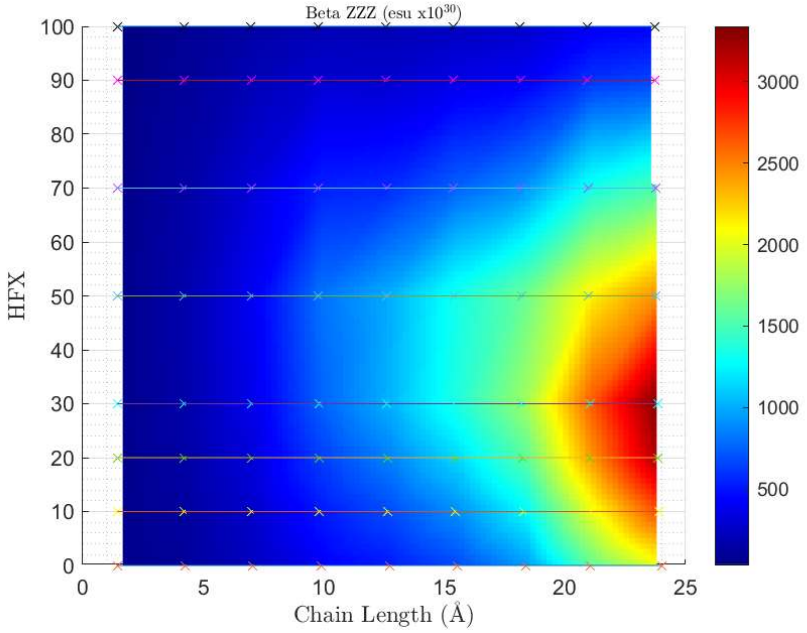
Bredas, J 1994, 'Experimental Demonstration of the Dependence of the First Hyperpolarizability of Donor-Acceptor-Substituted Polyenes on the Ground-State Polarization and Bond Length Alternations', *J. Am. Chem. Soc. 116* (6), 2619-2620

Conclusions

Conclusions

- Nonlinear response of performance-determining parameters to varied HFX suggests size-dependence of percent HFX needed to accurately model OEO chromophores/CT systems.





Impacts

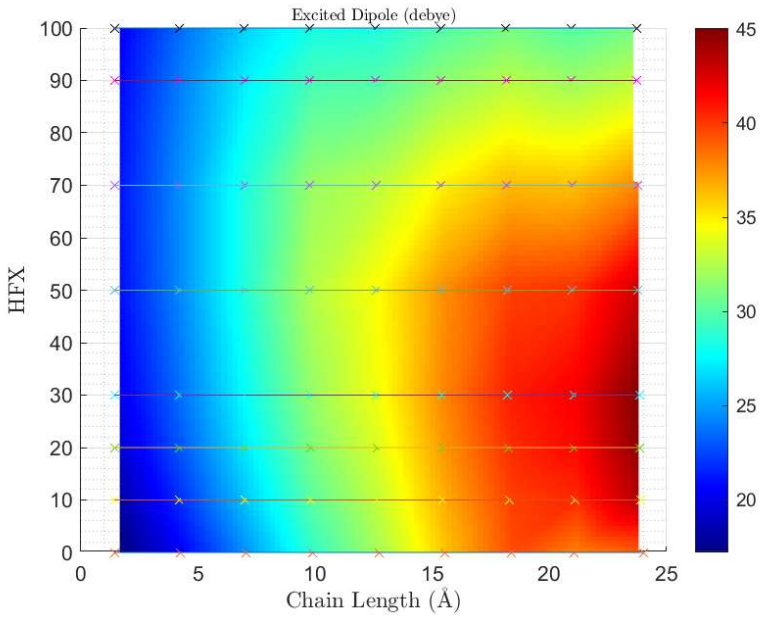
- Demonstration of size-extensivity of HFX has significant implications for calculations involving charge transfer systems and DFT functional design in general.
  - More accurate modelling of CT systems
    - Improved theory-driven design of organic electro-optic (OEO) chromophores
  - Reduction of systemic error in hybrid DFT calculations
    - Benefits any who regularly use DFT (many!)
      - "… Density functional theory, easily the most heavily cited concept in the physical sciences. Twelve papers on the top-100 list relate to it, including 2 of the top 10." – Nature

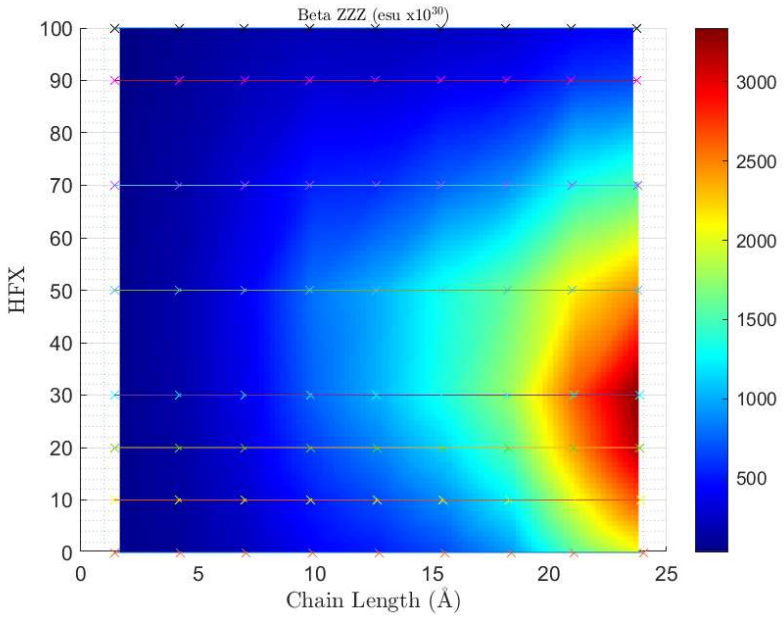
Van Noorden, Richard, 2014, 'The Top 100 Papers', *Nature*

Future Work

Future Work – Multivariate Data Analysis

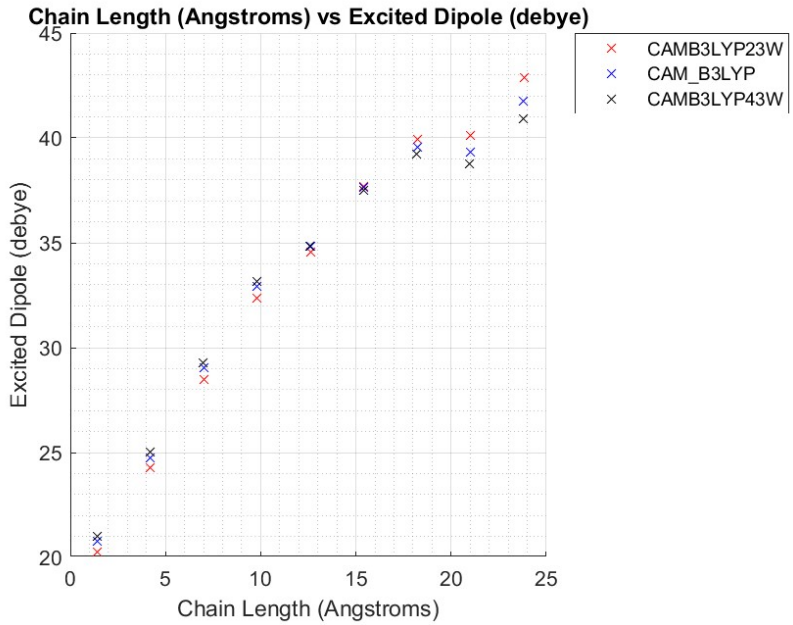
- Increase complexity of multivariate analysis of key molecular properties
  - Qualitative → Quantitative analysis. Determine *extent* of size-extensivity.

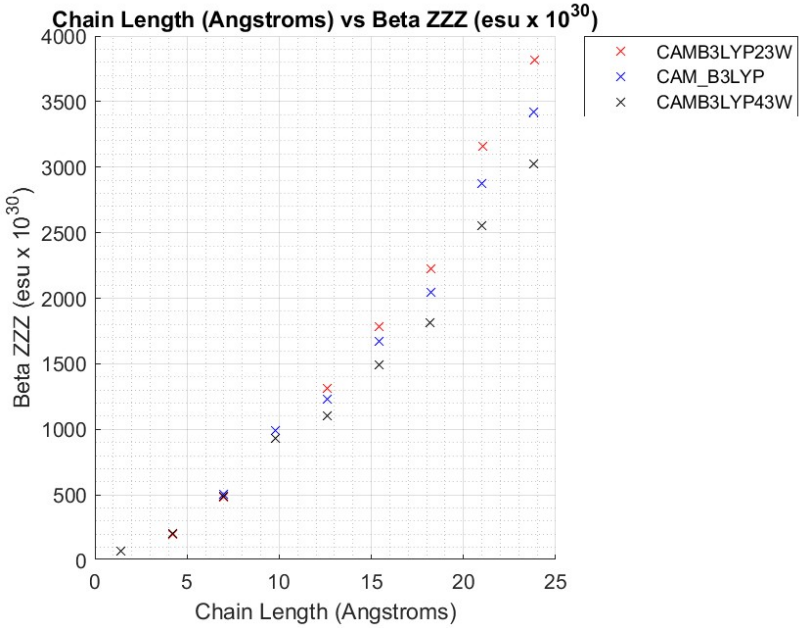




Future Work – Range-separated functionals

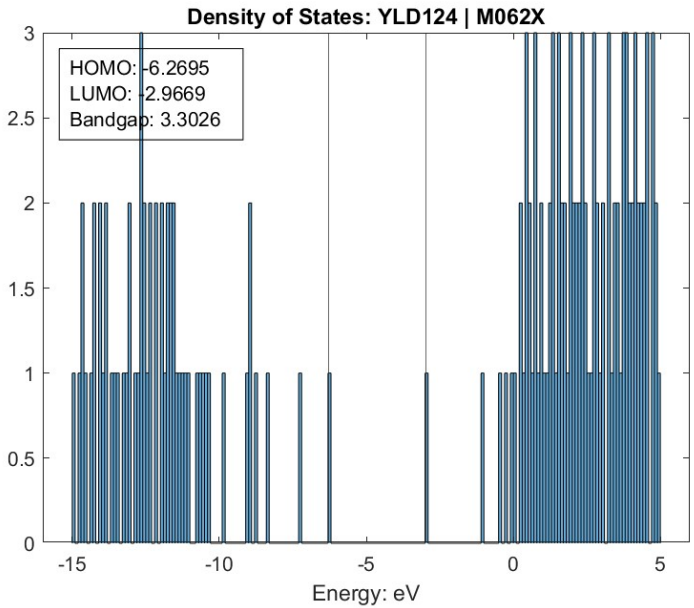
- Ex CAM-B3LYP -- %HFX varies from 20-65% depending on distance of interaction
  - Some calculations varying parameters of CAM-B3LYP transfer function complete

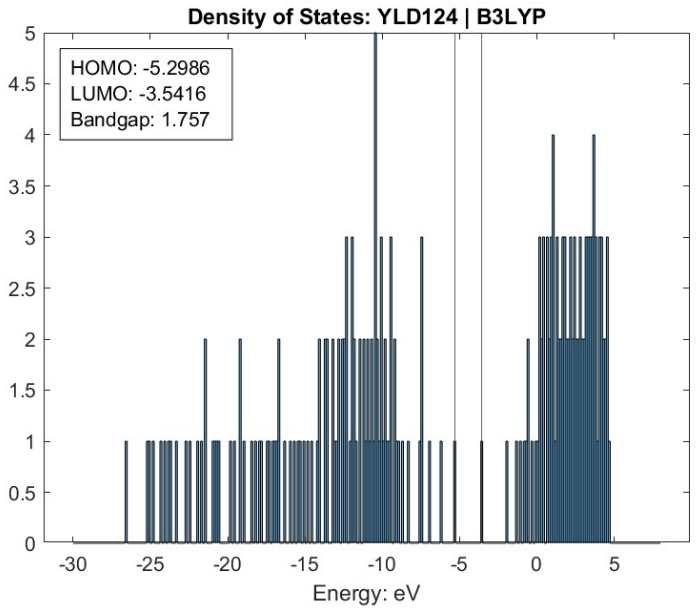




Future Work – Density of States Analysis

- Count participating pi electrons near HOMO – upper limit on hyperpolarizability
- Raw → Projected D.o.S., allows for programmatic analysis instead of manual brute-force analysis





Kuzyk, M 2009, 'Using fundamental principles to understand and optimize nonlinear-optical materials', *Journal of Materials Chemistry*

Questions?