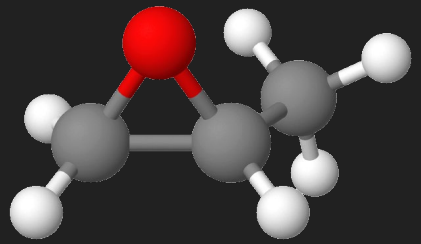
Calculation of Ionization Asymmetries in Chiral Molecules

Corbin Allison

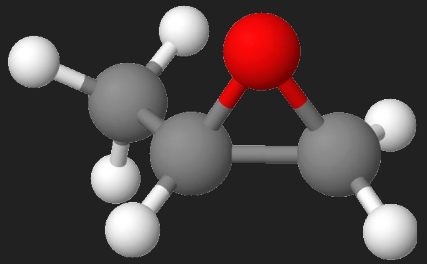
Chirality

- A molecule that cannot be superimposed onto its mirror image
  - Distinct images called enantiomers

R-enantiomer



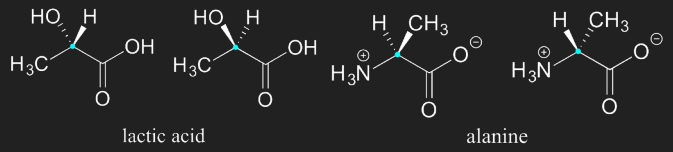
S-enantiomer

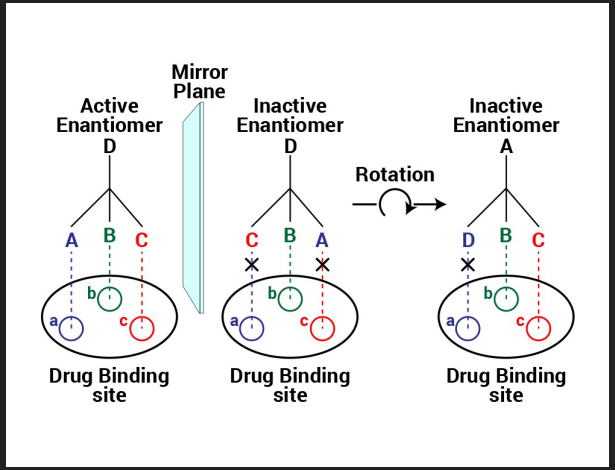


Propylene oxide (methyloxirane), made with MolView

Chiral Analysis

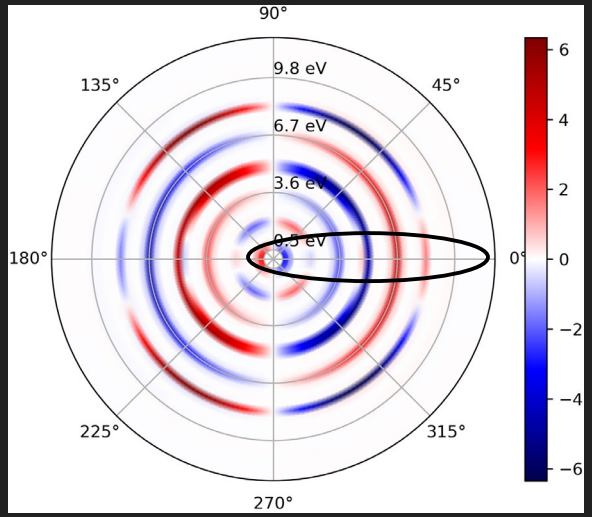
- Most biological molecules are chiral
- Ratio of enantiomers in a solution (enantiomeric excess) can be vital for drug synthesis
- Traditionally measured through absorption based measurements
  - Relatively weak signal



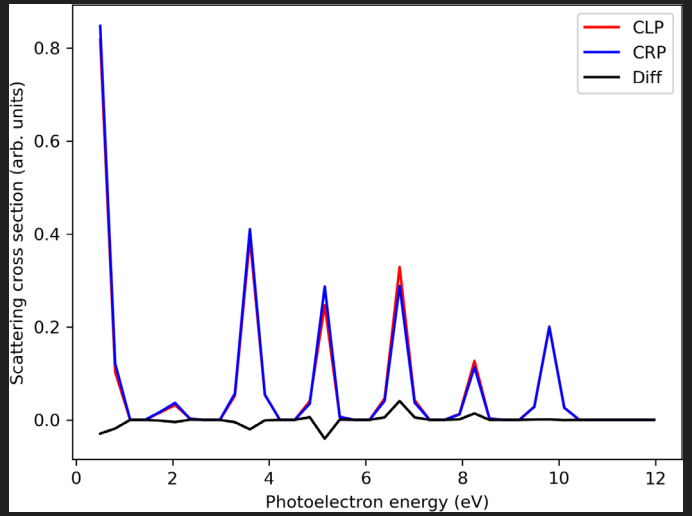


Photoelectron Circular Dichroism

- Chiral molecules will interact differently with different polarizations of light
- Circular dichroism: difference between interaction with CRP and CLP
- PECD measures angular distributions of photoelectrons



(with normalization)



Calculating PECD

1. Quantum chemistry: used to obtain the molecular orbitals
2. Scattering calculation: describes continuum states after ionization
3. Time-dependent perturbation theory: describes interaction with time-dependent field

- Solves for coefficients in the *N*-electron wave function

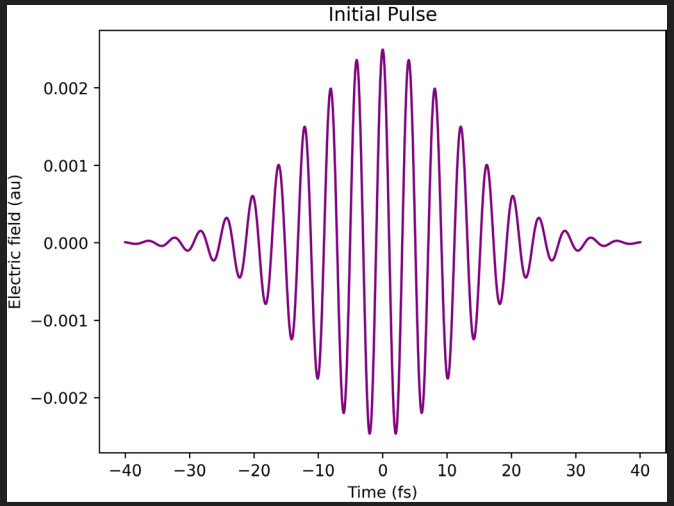
$$\left|\Psi^N(t)\right\rangle = \alpha_0(t)e^{-i\varepsilon_0 t}\left|\Phi_0\right\rangle + \sum_{i,a}\alpha_i^a(t)e^{-i\varepsilon_i^a t}\left|\Phi_i^a\right\rangle + \sum_i\int d\boldsymbol{k}\alpha_i^{\boldsymbol{k}}(t)e^{-i\varepsilon_i^{\boldsymbol{k}} t}\left|\Phi_i^{\boldsymbol{k}}\right\rangle$$

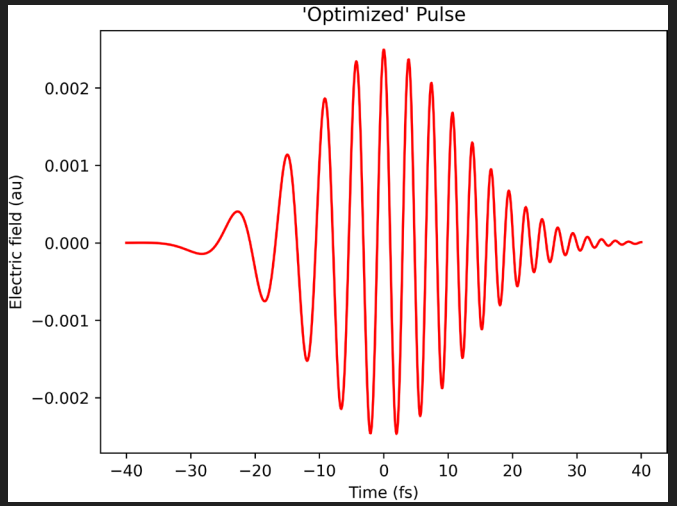
- Momentum distribution

$$\frac{d^2\sigma}{d\epsilon_k d\Omega_{\boldsymbol{k}'}} = \sum_{i\in\mathrm{occ}}\int\left|\alpha_i^{\boldsymbol{k}'}(t;\gamma_{\mathcal{R}})\right|^2 d^3\gamma_{\mathcal{R}} = \sum_{\ell,m}\beta_{\ell,m}(\epsilon_k)P_\ell^m(\cos\theta)e^{im\phi}$$

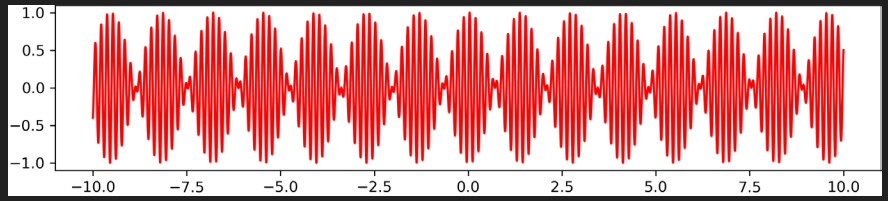
Quantum Control

- The driving field parameters (frequency, amplitude, etc.) are optimized for maximal PECD yields

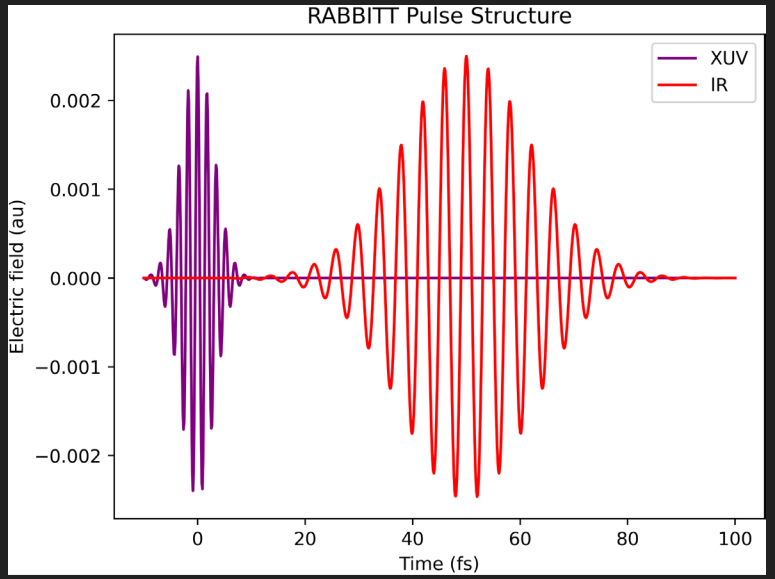


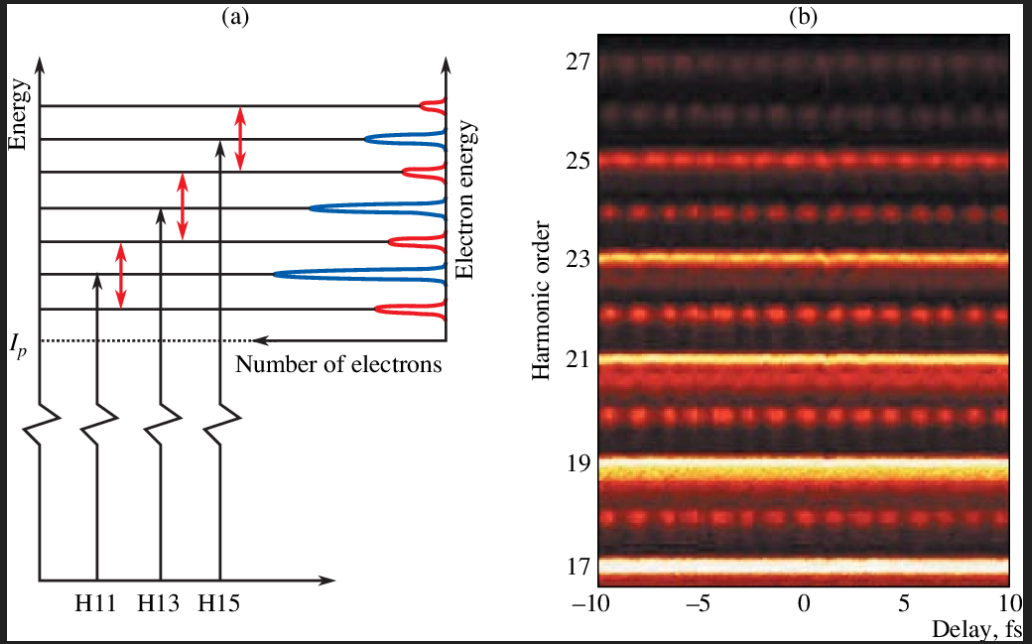


RABBITT



- Allows control of experimentally attainable pulses through relative delay

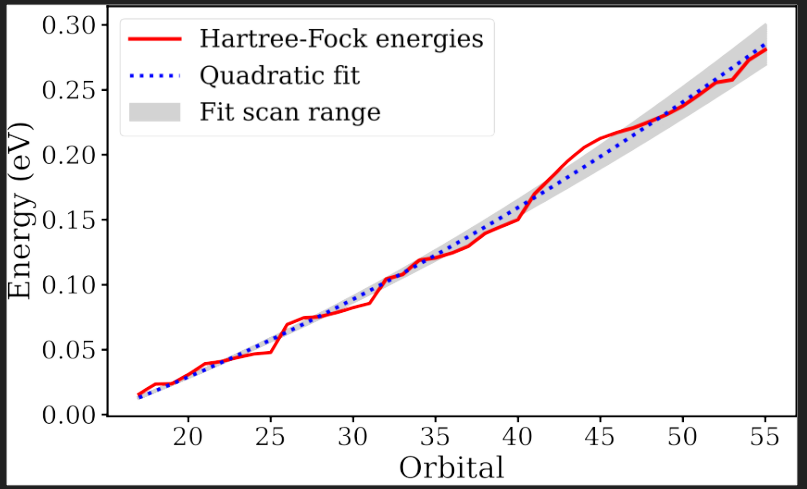




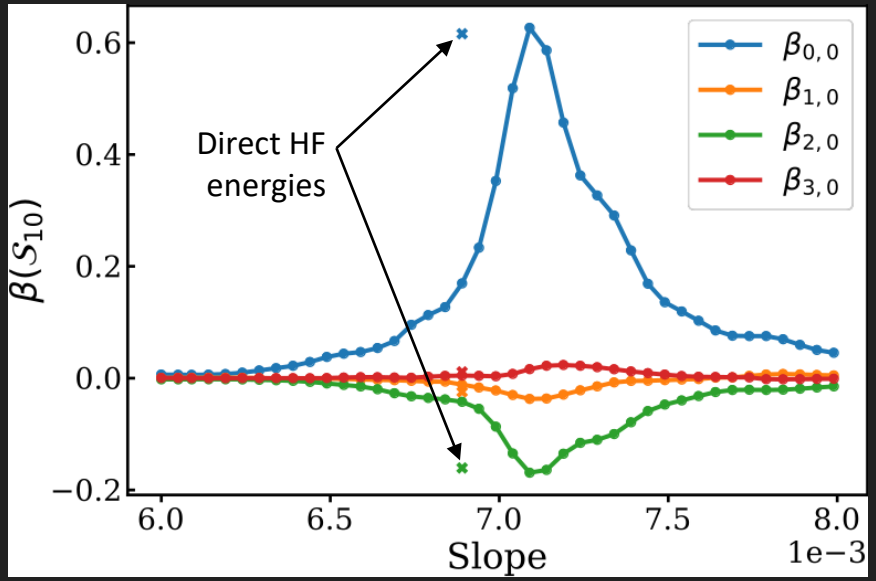
K.Varj´u et al., LASER PHYSICS (2005)

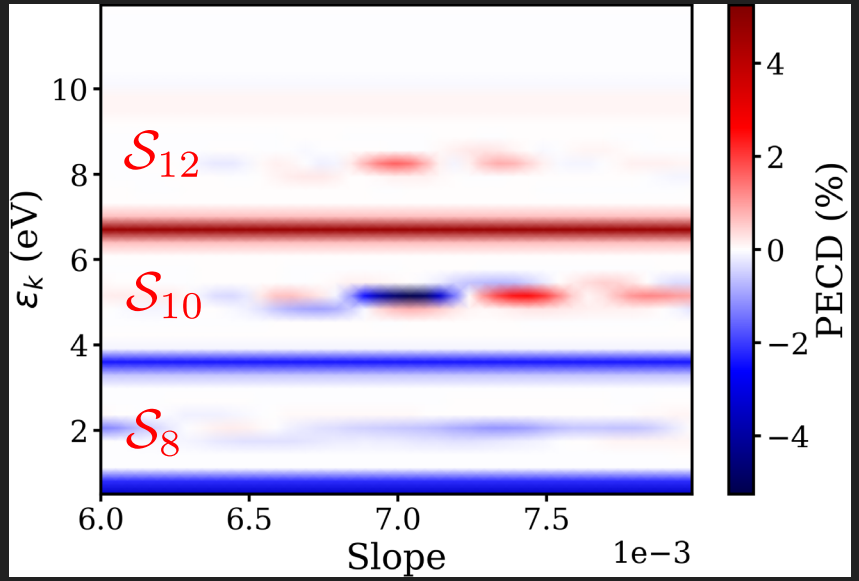
Quantum Chemistry Sensitivity

- Determine robustness of calculation
- Virtual orbital energies from quantum chemistry are fit using linear and quadratic fit
  - Anisotropy parameters, PECD calculated as function of varying fit parameters
- Imaginary components are also added

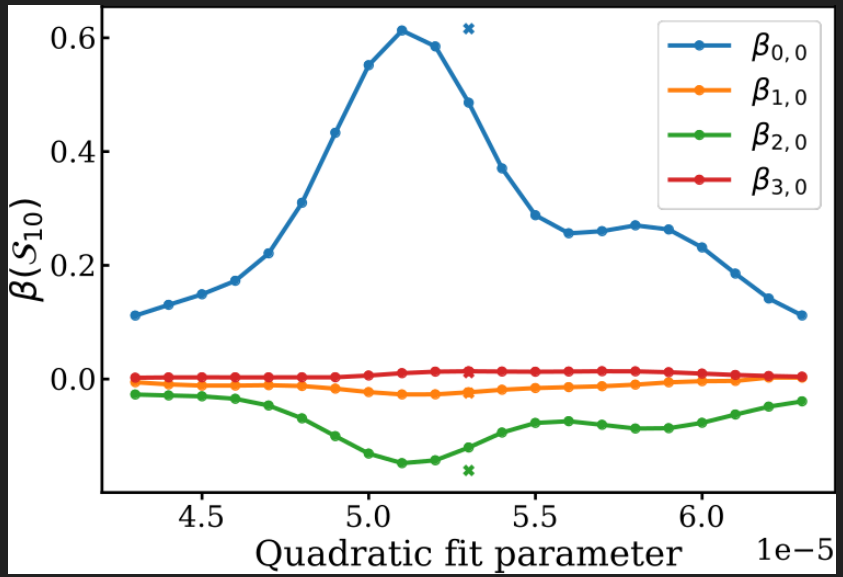


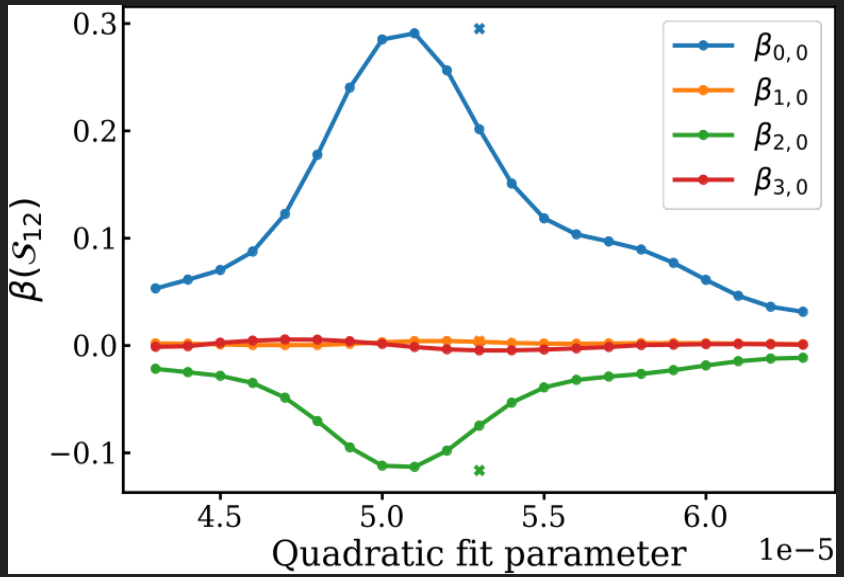
Slope Fit


Direct HF
energies
$\beta_{0,0}$
$\beta_{1,0}$
$\beta_{2,0}$
$\beta_{3,0}$
$\beta(\mathcal{S}_{10})$
0.6
0.4
0.2
0.0
−0.2
6.0
6.5
7.0
7.5
8.0
Slope
1e−3

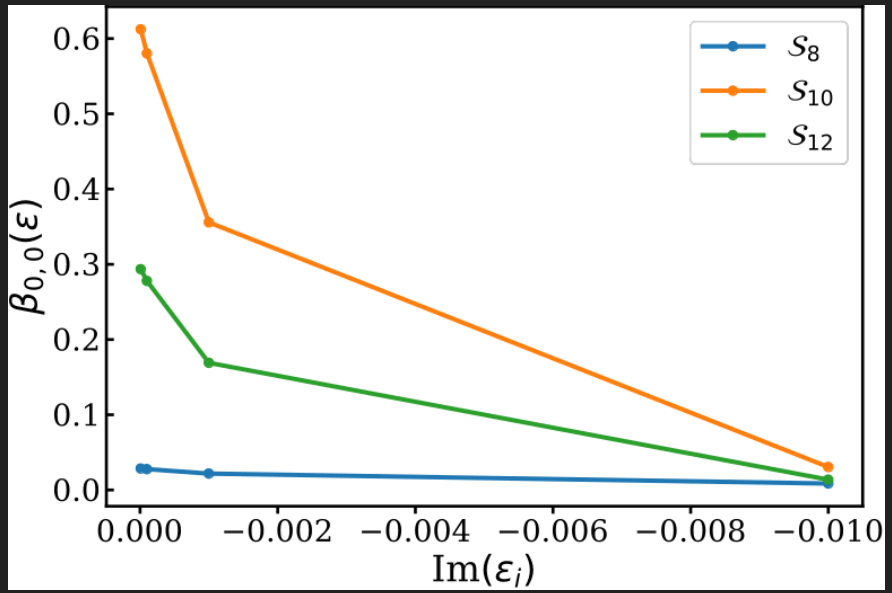

$\mathcal{S}_{12}$
$\mathcal{S}_{10}$
$\mathcal{S}_{8}$
ε_k (eV)
10
8
6
4
2
6.0
6.5
7.0
7.5
Slope
1e−3
4
2
0
−2
−4
PECD (%)

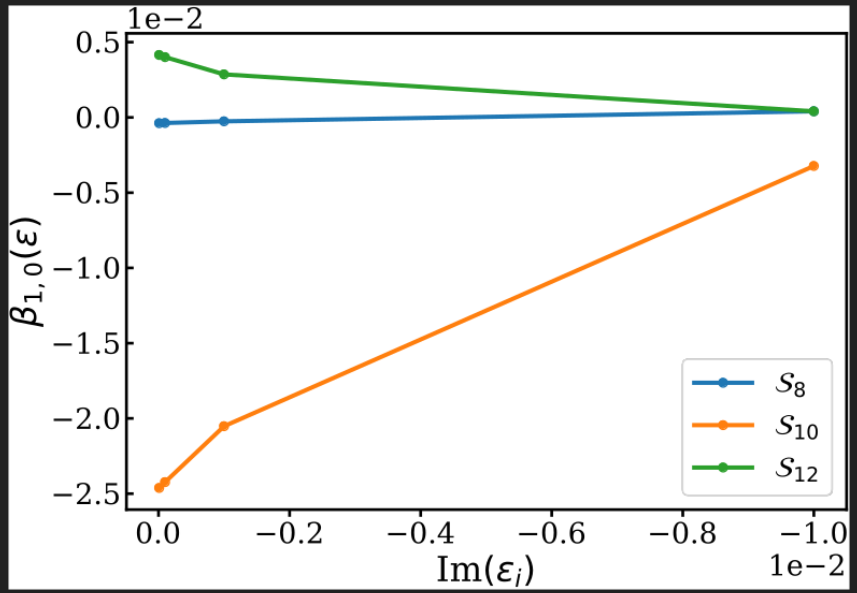
Quadratic Fit





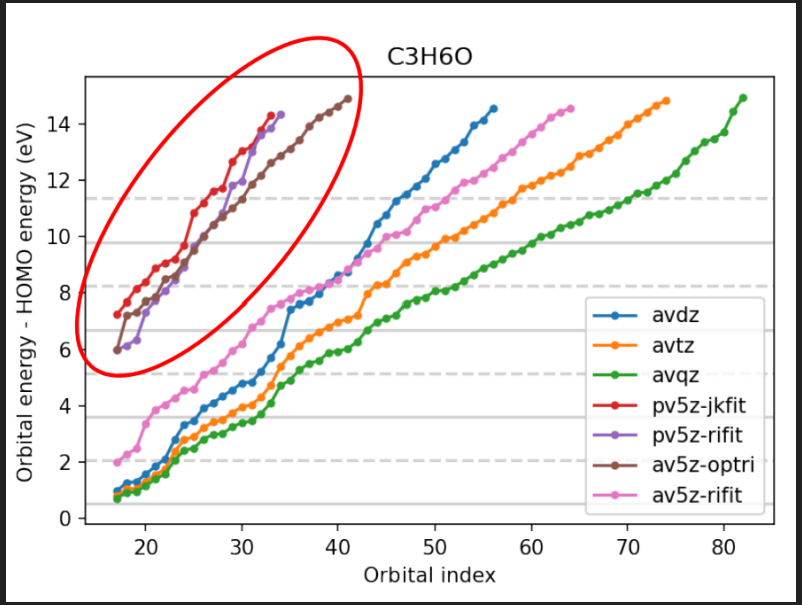
Complex ε_i





Conclusions

- PECD signals in RABBITT sidebands are sensitive to virtual orbital energies
- Sensitivity is present in anisotropy parameters
- Imaginary parts can be added to damp anisotropy parameters



Acknowledgements

- Kim Coy, Loren Greenman, JT Laverty, and the NSF
- Kansas State University
- Our collaborators:
  - UConn: E Goetz
  - Freie Universitat Berlin: C Koch and A Blech
  - ETH Zürich: M Han, HJ Wörner, and JB Ji

This material is based upon work supported by the National Science Foundation under Grant No. #2244539. Any opinions, findings, and conclusions or recommendations expressed in this material are those of the author(s) and do not necessarily reflect the views of the National Science Foundation.

Computations for this project were performed on Beocat Research Cluster at Kansas State University, and used resources of the National Energy Research Scientific Computing Center (NERSC)