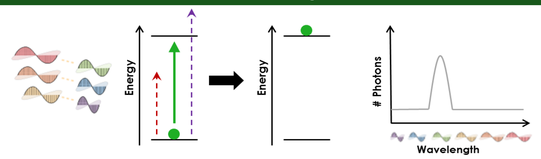
Effect of Basis Sets on Absorbance Spectra

Sarah Zinn (Ohio Northern University) s-zinn@onu.edu
Selina Arrington-Boyd (North Carolina Central University) sarrin11@eagles.nccu.edu
Mentors: Jacek Jakowski (ORNL) jakowskij@ornl.gov; Shi-Quan Su (ORNL) ssu2@utk.edu

Overview

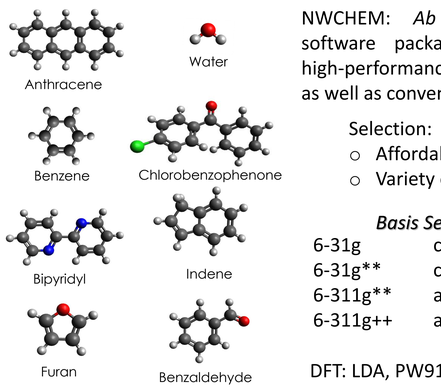
Understanding accuracy and predictive capabilities of theoretical models in simulation of absorption spectra is important for design of new light-absorbing devices such as solar cells. DFT based approaches allow for inexpensive simulation of absorption but the accuracy strongly depends on the basis set and functional used. By exploring the theoretical simulations of absorbance spectra utilizing NWChem, we can understand the nature of absorbance energy shift as it correlates with basis set completeness.[1,2]

Absorbance Spectra



- Selective absorption of light
- energy difference between the ground and excited states

Methods



NWCHEM: *Ab initio* chemistry software package. Designed for high-performance super computers as well as conventional clusters.

Selection:
- Affordable molecules
- Variety of basis sets

Basis Sets

6-31g	cc-pVTZ
6-31g**	cc-pVDZ
6-311g**	aug-cc-pVTZ
6-311g++	aug-cc-pVDZ

DFT: LDA, PW91, PBE, B3LYP

TD-DFT[4]

A Quantum mechanical method used to study properties and dynamics of many-body systems in external, time-dependent perturbations.

- **Real-Time (RT) TD-DFT**: time domain
- **Linear Response (LR) TD-DFT**: frequency domain; real-time (RT) TD-DFT with LR TD-DFT
  - ***Casida Equation*** (Random Phase Approximation), RPA

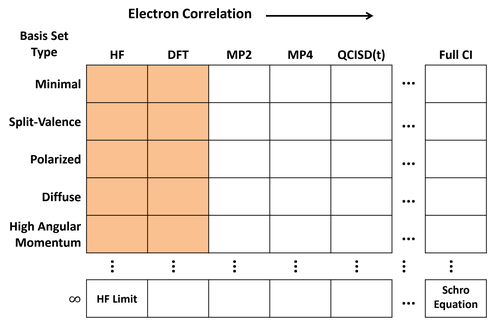
$$\begin{pmatrix} -A & -B \\ B & A \end{pmatrix} \begin{pmatrix} x' \\ y' \end{pmatrix} = i\hbar\omega \begin{pmatrix} x' \\ y' \end{pmatrix}$$

  - ***Tamm-Dancoff Approximation*** (some elements in B dropped, leads to a worse approximation)

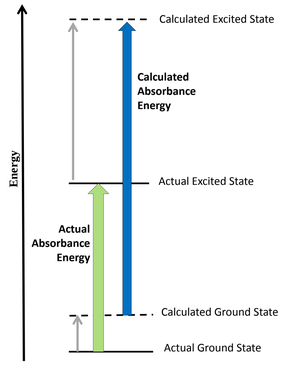
Direct approach: Solve TD Schrödinger equation of the many-electron wave function

$$i\hbar \frac{\partial}{\partial t} |\Psi(t)\rangle = (H + V)|\Psi(t)\rangle$$

Our Work

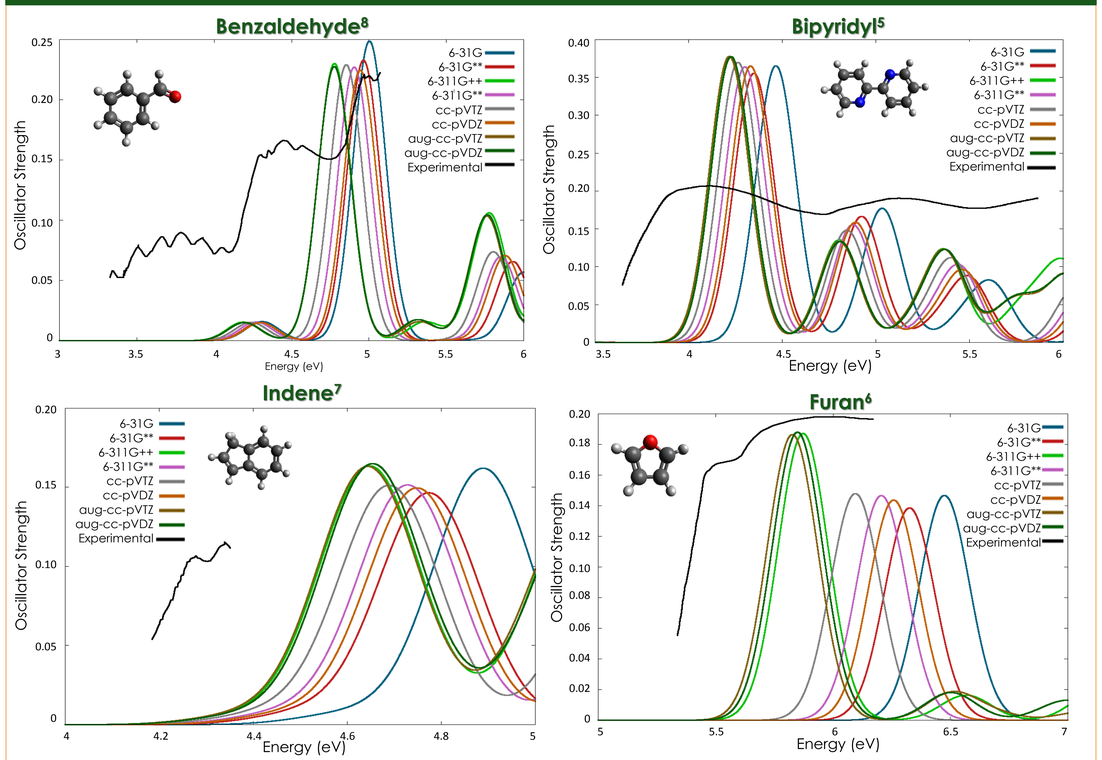


- A set of functions combined in linear combinations to create molecular orbitals
- The larger and more complex a basis set is, the better the approximation of energy.



- Calculated state energies are bound
- Ground state energies converge faster than ground state energies
- Goal: To determine how complete of a basis set is necessary to see convergence of absorbance energies.

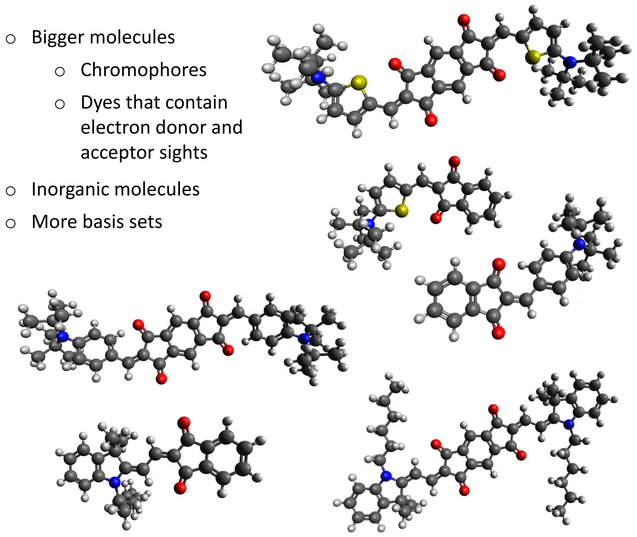
Results and Conclusions



- All data sets analyzed appear to have red shifted absorbance peaks with increasing basis set size.
- As a general trend, we saw convergence of augmented basis sets. However, smaller basis sets remained reasonably close to the augmented basis sets (with the exception of 6-31G)
- Most data was agreeable with experimental UV-Vis data (within 0.2 to 0.5 eV) which is within an acceptable tolerance of real data.
- While we saw convergence with augmented data, it may be more computationally efficient to calculate absorbance spectra with smaller basis sets, like cc-pVTZ

Future Work

- Bigger molecules
  - Chromophores
  - Dyes that contain electron donor and acceptor sights
- Inorganic molecules
- More basis sets



Computational Parameters

Geometry Optimization

Qchem 4.1
DFT/B3LYP
Basis: LANL2DZ

Absorbance Spectra Calculations

Machine: NICS Darter
TD-DFT in NWChem 6.3
DFT / PBE96
Basis Sets: Pople, Dunning

References

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