

# Effect of Basis Sets on Absorbance Spectra

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## Overview

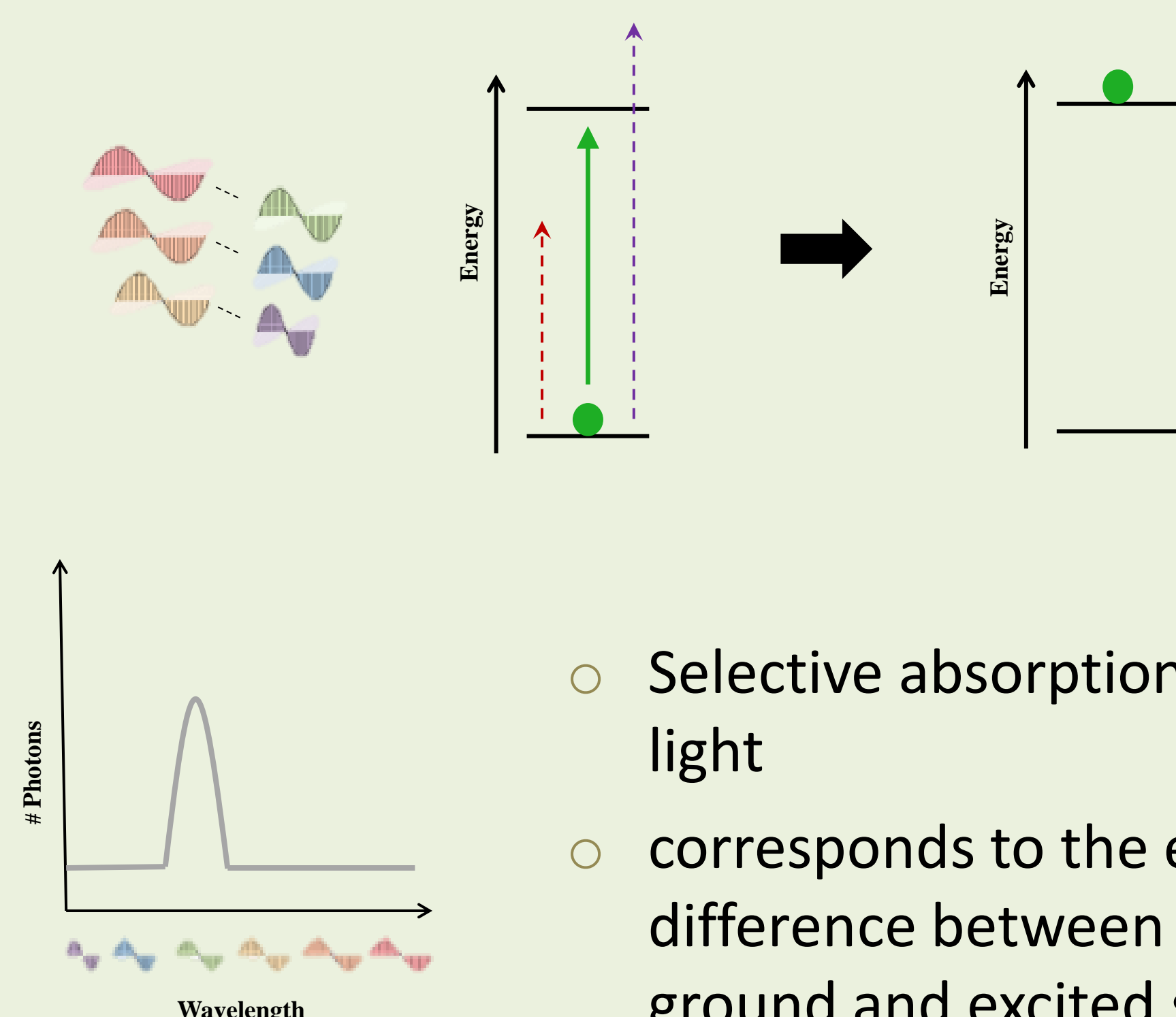
Understanding accuracy and predictive capabilities of theoretical models in simulation of absorption spectra is important for design of new light-absorbing devices such as solar cells. DFT based approaches allow for inexpensive simulation of absorption but the accuracy strongly depends on the basis set and functional used. A combined electronic structure and high-throughput tools, such as swift, allow for systematic studies of basis set effect in popular DFT functionals for various molecules. <sup>1,2</sup>

## NWChem<sup>3</sup>



- Ab initio chemistry software package
- Designed for high-performance super computers as well as conventional clusters.
- Capabilities:** Molecular dynamics, Molecular Mechanics, HF (SCF), DFT, TD-DFT, P-HF, QM/MM, ONIOM

## Absorbance Spectra



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

## Basis Sets

Basis Set Type	Electron Correlation →					Full CI
	HF	DFT	MP2	MP4	QCISD(t)	
Minimal						...
Split-Valence						...
Polarized						...
Diffuse						...
High Angular Momentum						...
∞	HF Limit					Schrodinger Equation

- 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.
- Balance computational cost with accuracy

## TD-DFT<sup>4</sup>

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

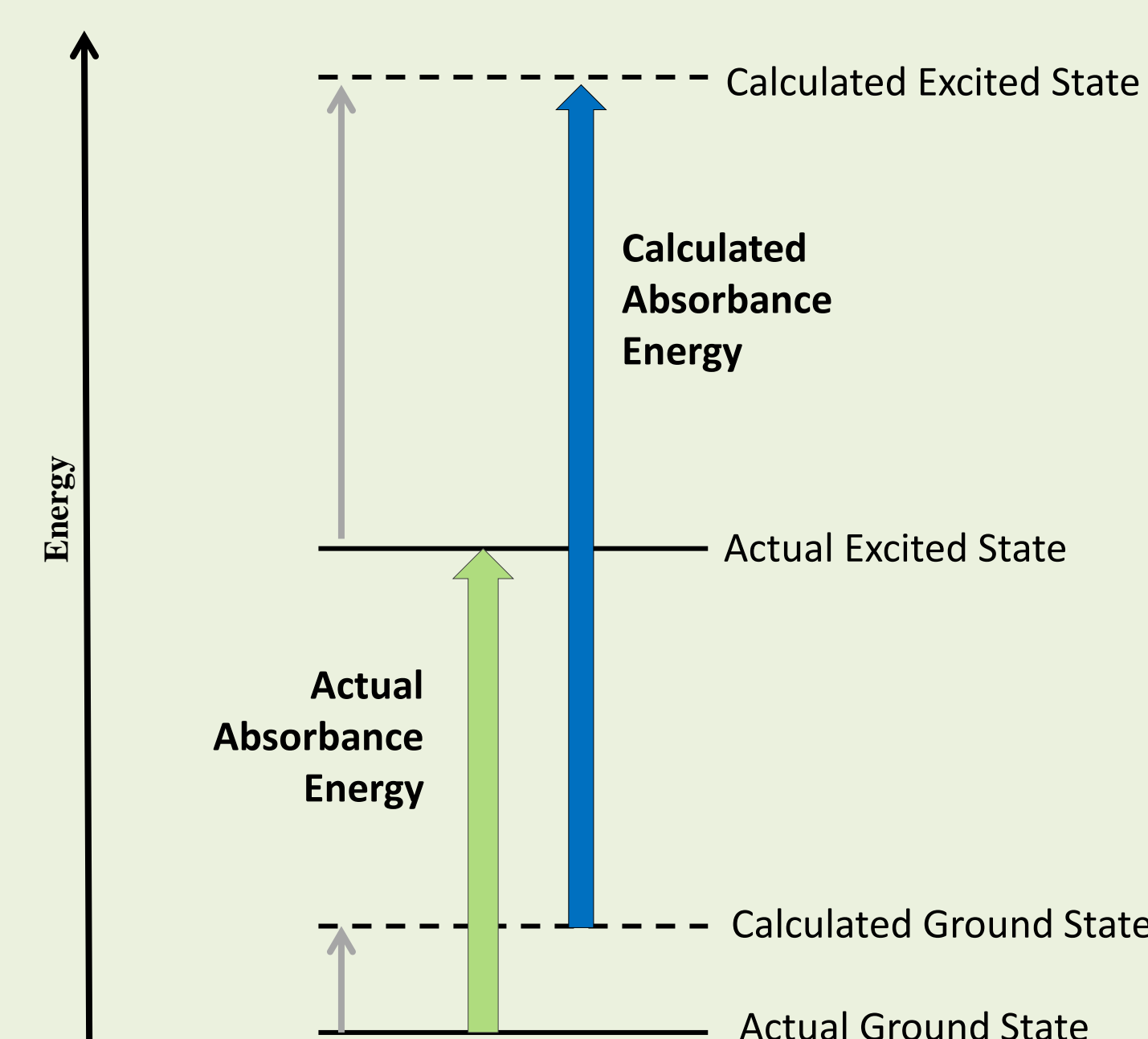
$$\begin{pmatrix} -A & -B \\ B & A \end{pmatrix} \begin{pmatrix} x' \\ y' \end{pmatrix} = i\hbar\omega \begin{pmatrix} x' \\ y' \end{pmatrix}$$

- Tamm-Dancoff Approximation** (some elements in B dropped)

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

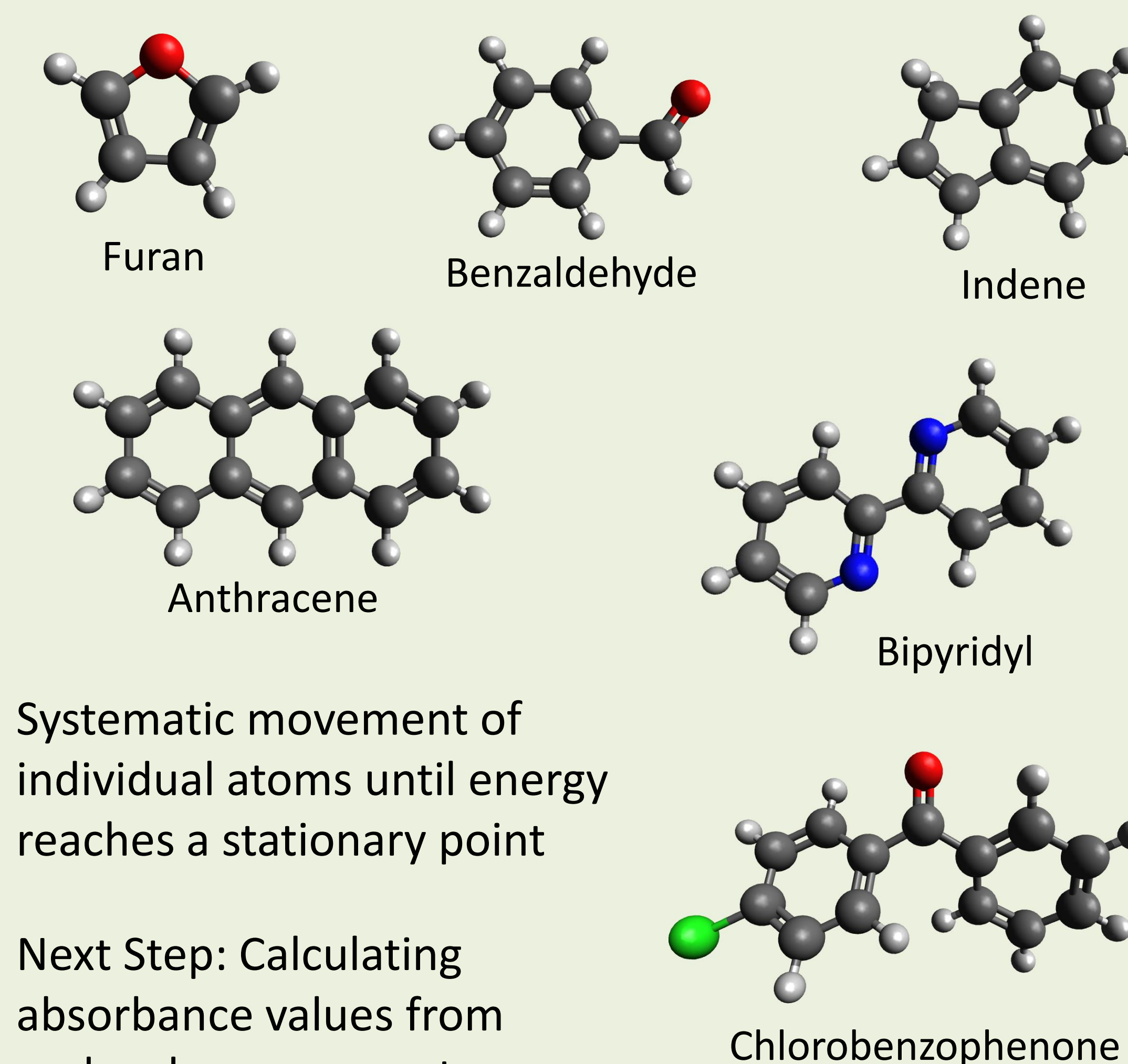
$$i\hbar \frac{\partial}{\partial t} |\Psi(t)\rangle = (H + V)|\Psi(t)\rangle$$

## Our Work



- Calculated state energies are bound (always higher)
- Excited state energies converge faster than ground state energies
- Absorbance energies are the differences in energies.
- Goal: To determine how complete of a basis set is necessary to see convergence of absorbance energies.

## Progress



- Systematic movement of individual atoms until energy reaches a stationary point
- Next Step: Calculating absorbance values from molecular movements.

## Computational Parameters

### Geometry Optimization

Qchem 4.1  
DFT/B3LYP  
Basis: LANL2DZ

### Future Absorbance Spectra Calculations

Machine: NICS Darter  
TD-DFT in NWChem 6.3  
Basis Sets: Pople, Dunning  
DFT: LDA, PW91, PBE, B3LYP

## References

- Jacquemin, D.; Perpète, E. A.; Scuseria, G. E.; Ciofini, I.; Adamo, C.; *J. Chem. Theory Comput.* **2008**, *4*, 123-135.
- Jacquemin, D.; Wathelet, V.; Perpète, E. A.; Adamo, C.; *J. Chem. Theory Comput.* **2009**, *5*, 2420-2435.
- M. Valiev, E.J. Bylaska, N. Govind, K. Kowalski, T.P. Straatsma, H.J.J. van Dam, D. Wang, J. Nieplocha, E. Apra, T.L. Windus, W.A. de Jong, *Comput. Phys. Commun.* **181**, 1477 (2010)
- Eberhard, K.; Gross, U.; Matira, N. T. Introduction to TDDFT. *Fundamental of Time-Dependent Density Functional Theory*. Springer Berlin Heidelberg: New York, 2012.

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