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National Organization for the Professional Advancement of Black Chemists and Chemical Engineers

Recent Applications of Orthogonality Constrained Density Functional Theory: Core Excitations

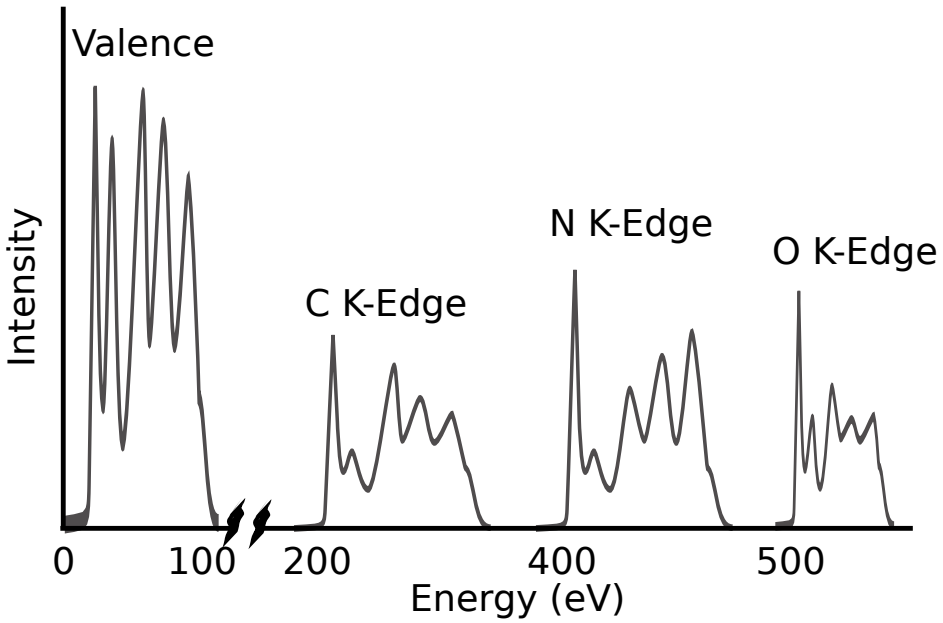
Wallace Derricotte, Prakash Verma, Francesco Evangelista

NOBCChE Presentation

Evangelista Lab

09/24/15

Core-Excited States



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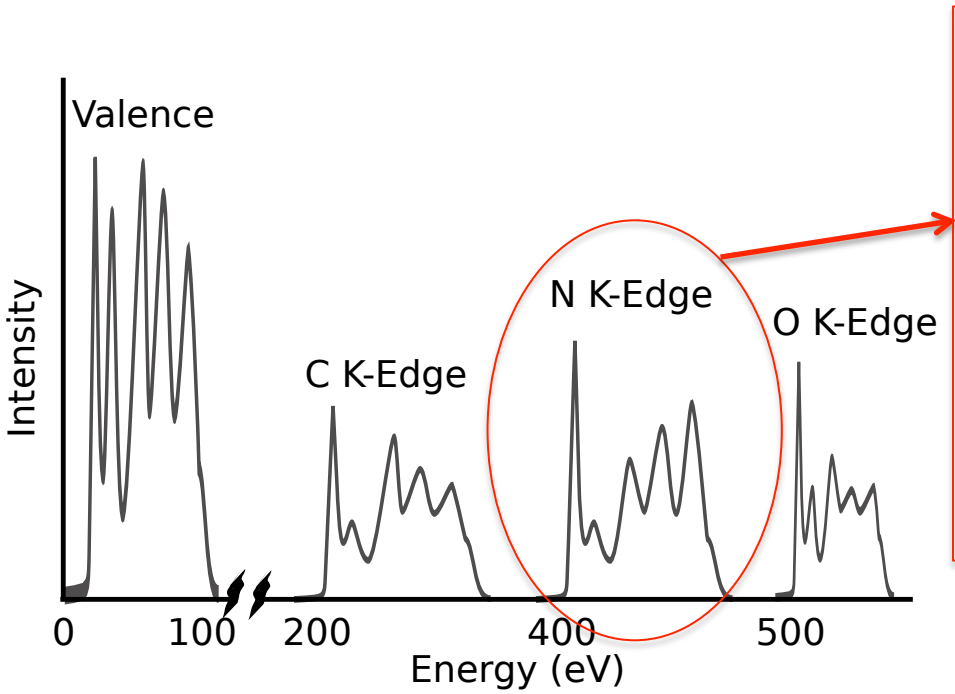

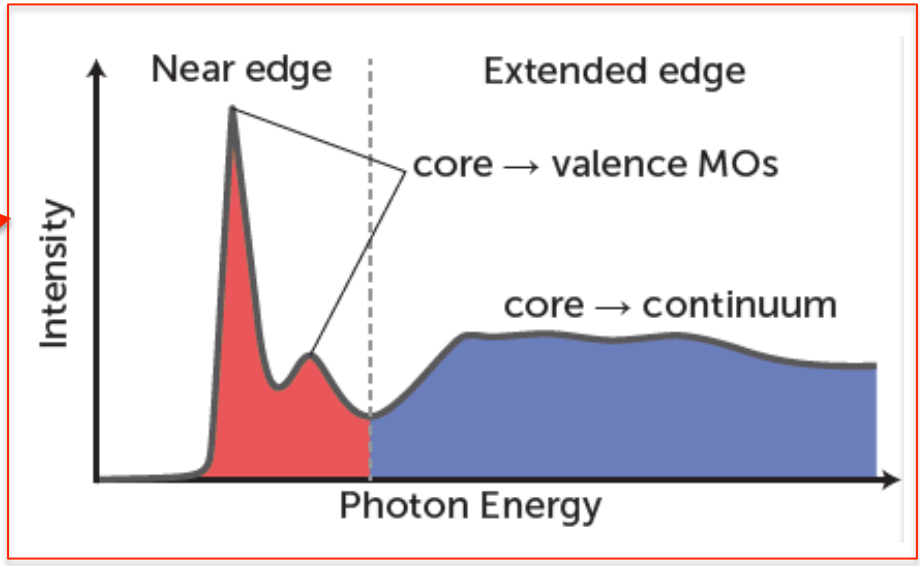

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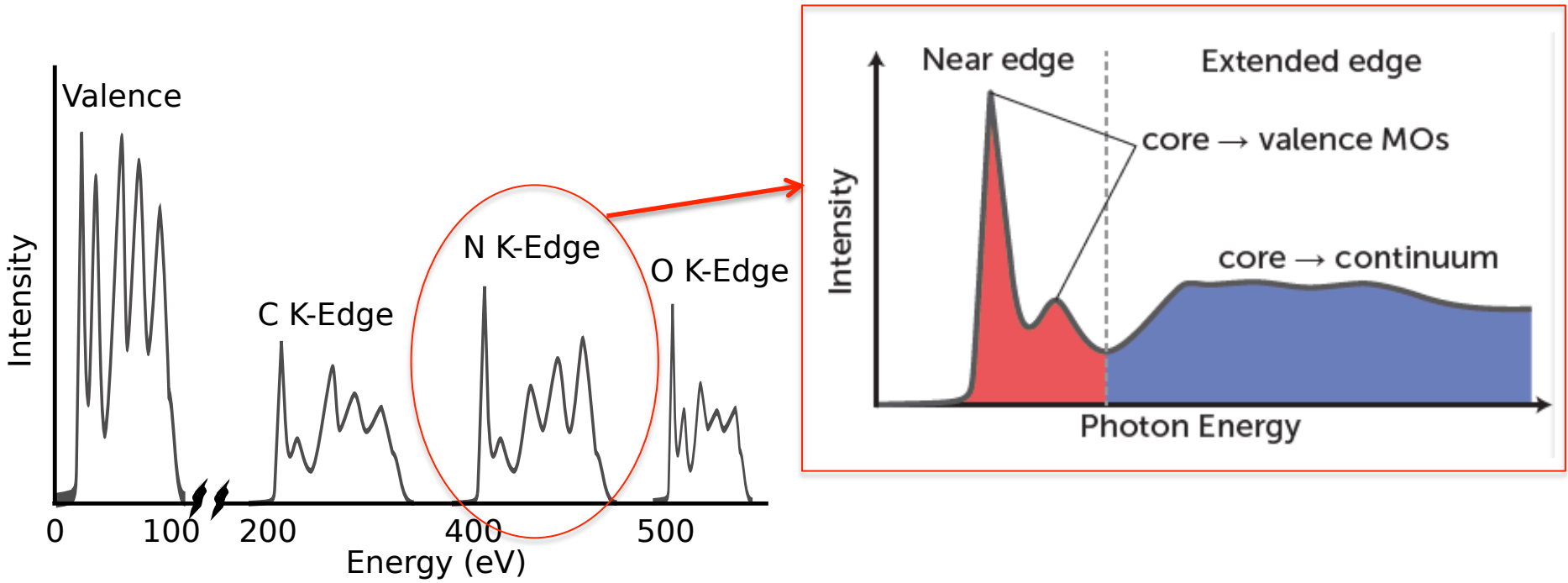

- Theoretical Challenges Include:
  - Orbital relaxation
  - Require treatment of scalar (1s excitations) and spin-dependent relativistic effects
  - Electron correlation

Computational Approaches

Wavefunction/Green's Function Methods

- SOS-CIS(D)[1]
- RASSCF[2]
- LR-CC methods[3]
- Algebraic Diagrammatic Construction (ADC)[4]

TDDFT

- Linear Response TDDFT[5]
- Real-Time TDDFT[6]
- ROKS/CIS[7]

Other Methods

- Static Exchange Approx. (IVO-HF)[8]
- Maximum Overlap ΔSCF[9]

1) Asmuruf, F.A.; Besley, N.A., *Chem. Phys. Lett.* **2008**
2) Ågren, H.; Jensen, H.J.A.; *Chem. Phys.* **1993**
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Accurate but Expensive

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More Economical but have limitations.

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Computationally Cheap, but inaccurate, requires energy shifts or SIC Functionals

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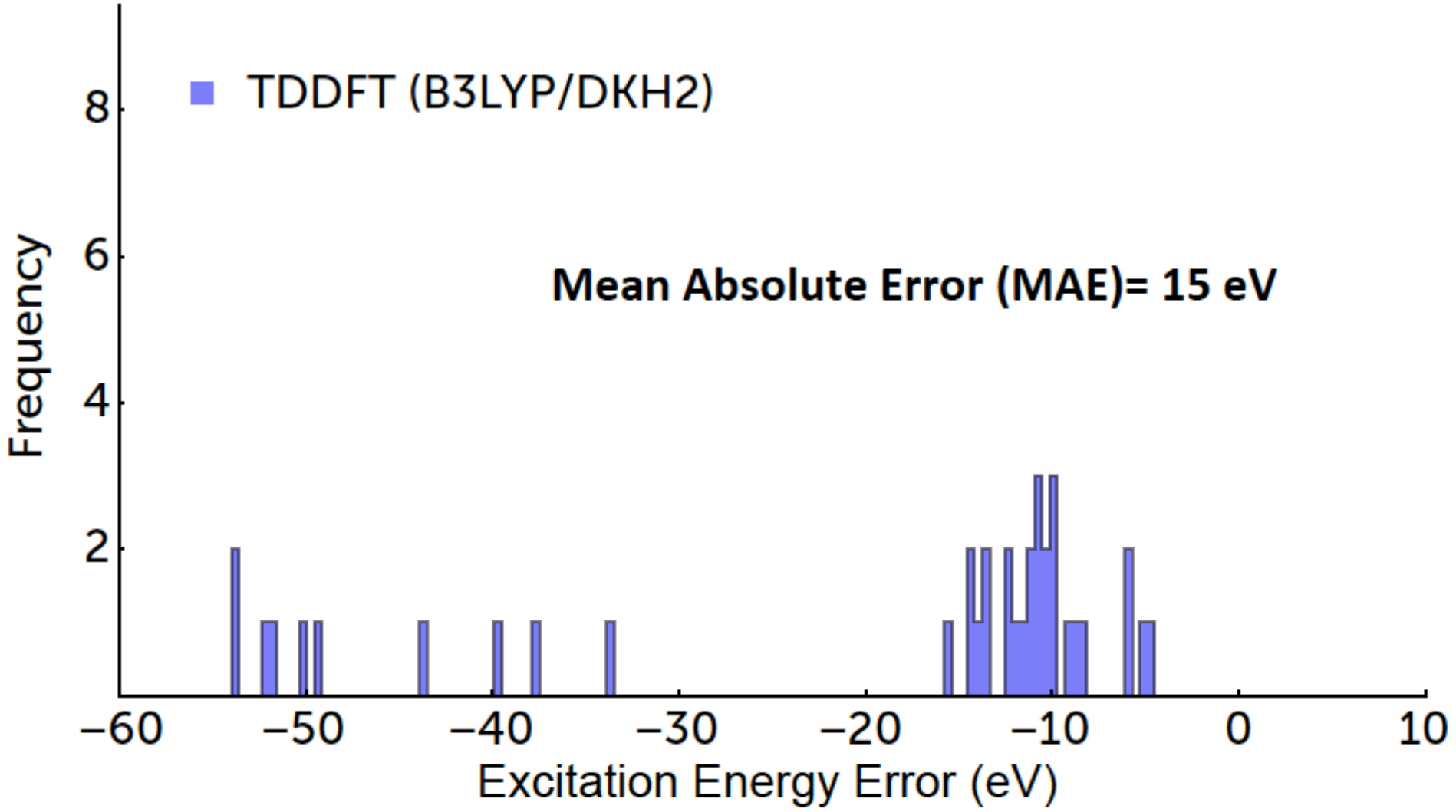
Core-Excited States With TDDFT



TEST SET → First-row elements: CO, H_2CO, N_2O, N_2, HCN, CH_4, C_2H_4

Second-row elements: SiH_4, PH_3, H_2S, SO_2, HCl, Cl_2

Compensating for Failure of TDDFT

- Standard functionals fail dramatically for core excitations, which results in a large underestimation of the excitation energy.
  - Poor performance stems the low quality of the KS eigenvalues, use of frequency independent XC functionals.
- It is common for TDDFT spectra to be shifted by a uniform amount in order to compensate for the underestimation.

Method	Avg. Energy Shift (eV)
BP86	171.1
B3LYP	143.3
BP86	171.0
BP86/DKH2	105.6

DeBeer George, S.; Petrenko, T.; Neese, F. *J. Phys. Chem. A* **2008**

Orthogonality Constrained Density Functional Theory (OCDFT)

- Variational time-independent formulation of DFT
  - Builds upon variational DFT approaches[1-7] but imposes an orthogonality condition on the Kohn-Sham system:

$$\left\langle \Phi^{(m)} \middle| \Phi^{(n)} \right\rangle = \delta_{mn}$$

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Avoids Variational Collapse

- OCDFT also introduces a quasi-adiabatic approximation in which the XC functional for each excited state is approximated as the ground state XC functional.

$$E^{(n)}_{\mathrm{OCDFT}}[\rho^{(n)}] = \sum_{\mu\nu} D^{n}_{\mu\nu}(T_{\mu\nu} + V_{\mu\nu}) + E_{\mathrm{coul}}[\rho^{(n)}] + E^{(0)}_{\mathrm{xc}}[\rho^{(n)}].$$

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Extension of OCDFT to Simulate NEXAS Spectra

- Must introduce two new features to OCDFT to calculate NEXAS spectra
  - Previous implementation selected the *highest lying* hole orbitals (highest hole eigenvalue) however for core excitations we want to select the *lowest lying* hole orbitals (lowest hole eigenvalue).
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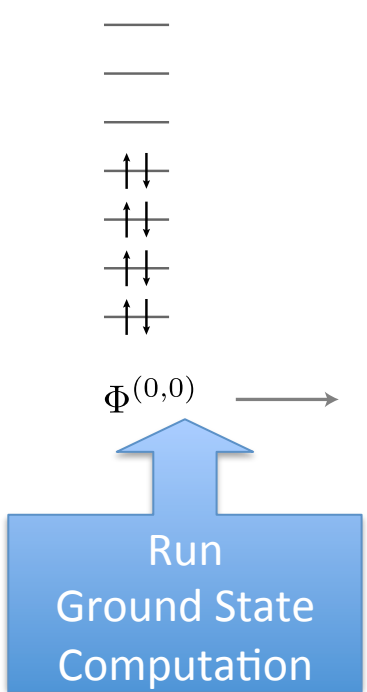

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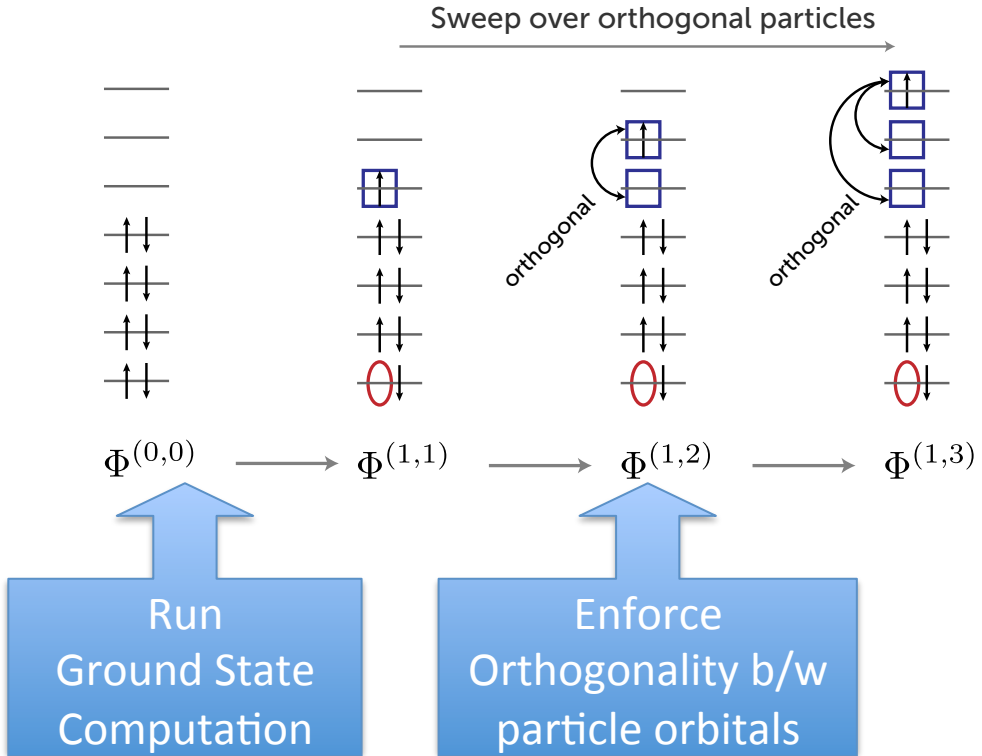

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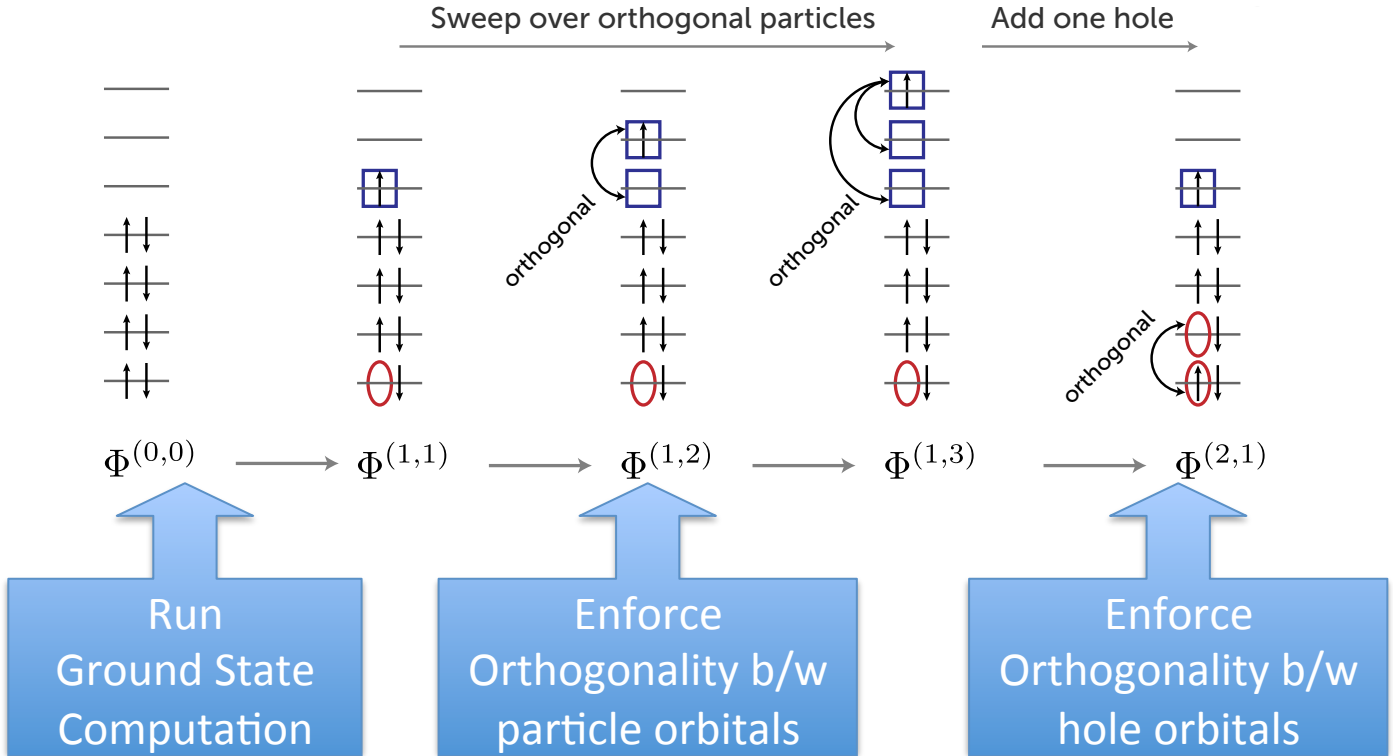

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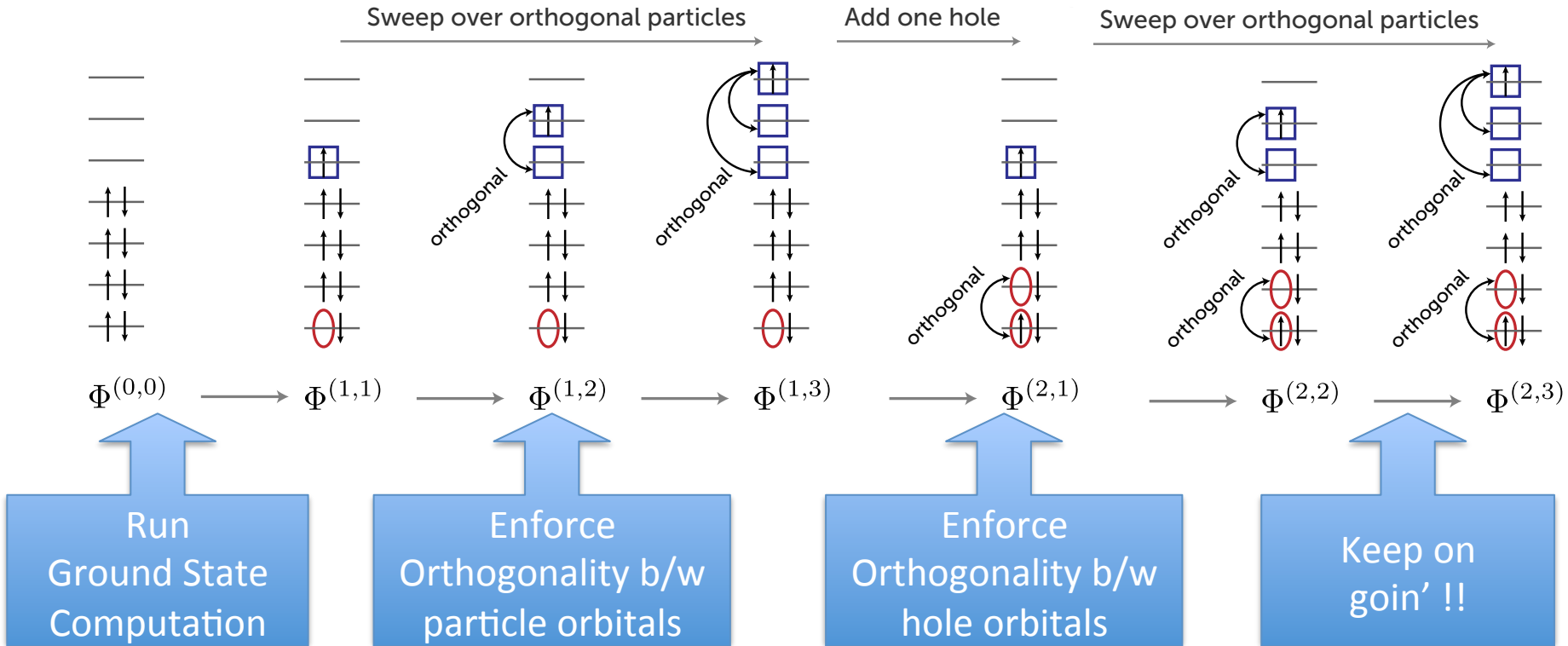
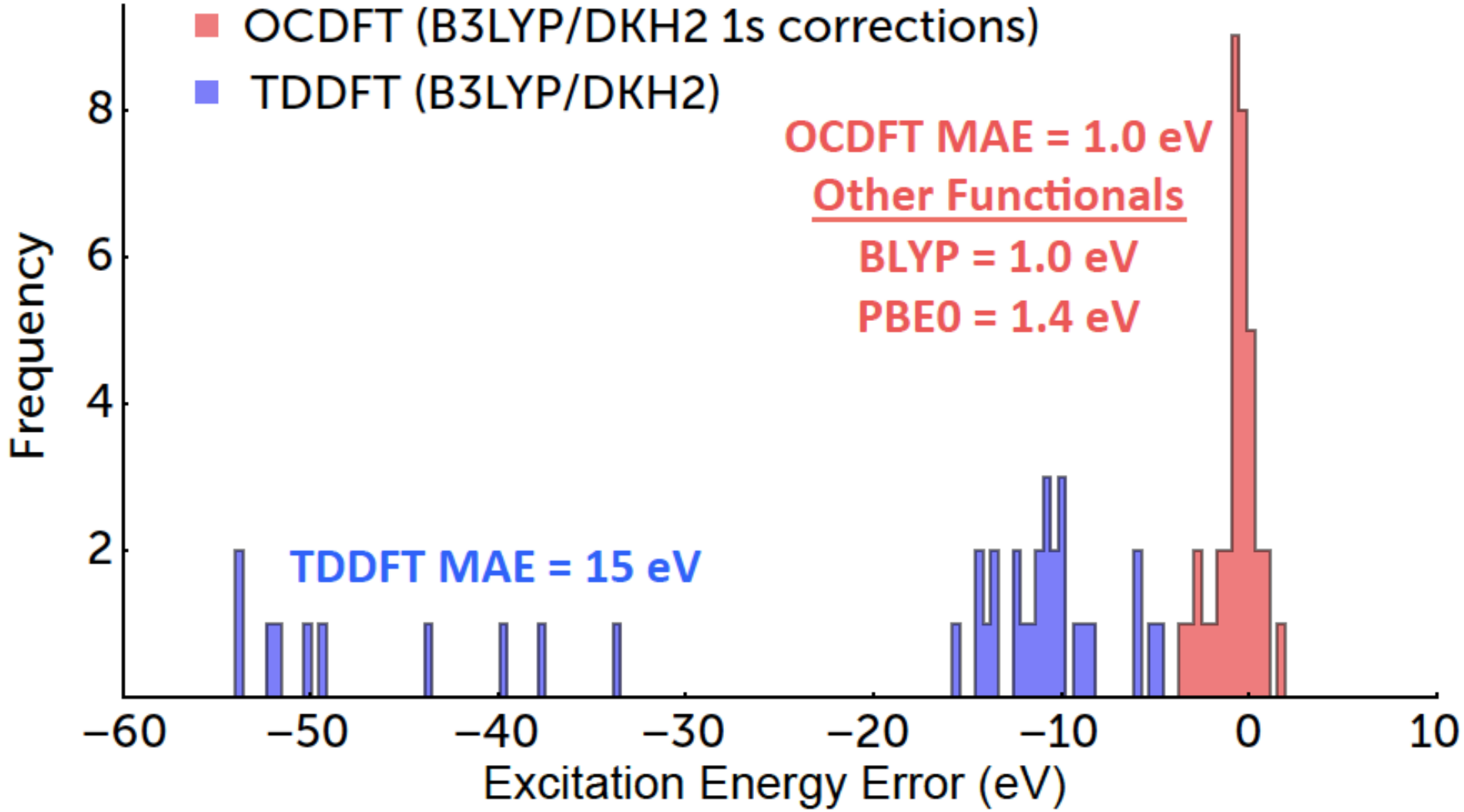


Comparison to TDDFT



- EOM-CCSD[1] (MAE) = 0.9 eV
- SOS-CIS(D)[2] [MAE] = 1.2 eV
- Max Error for OCDFT: -3.7 eV
- Max Error for TDDFT: -53.6 eV

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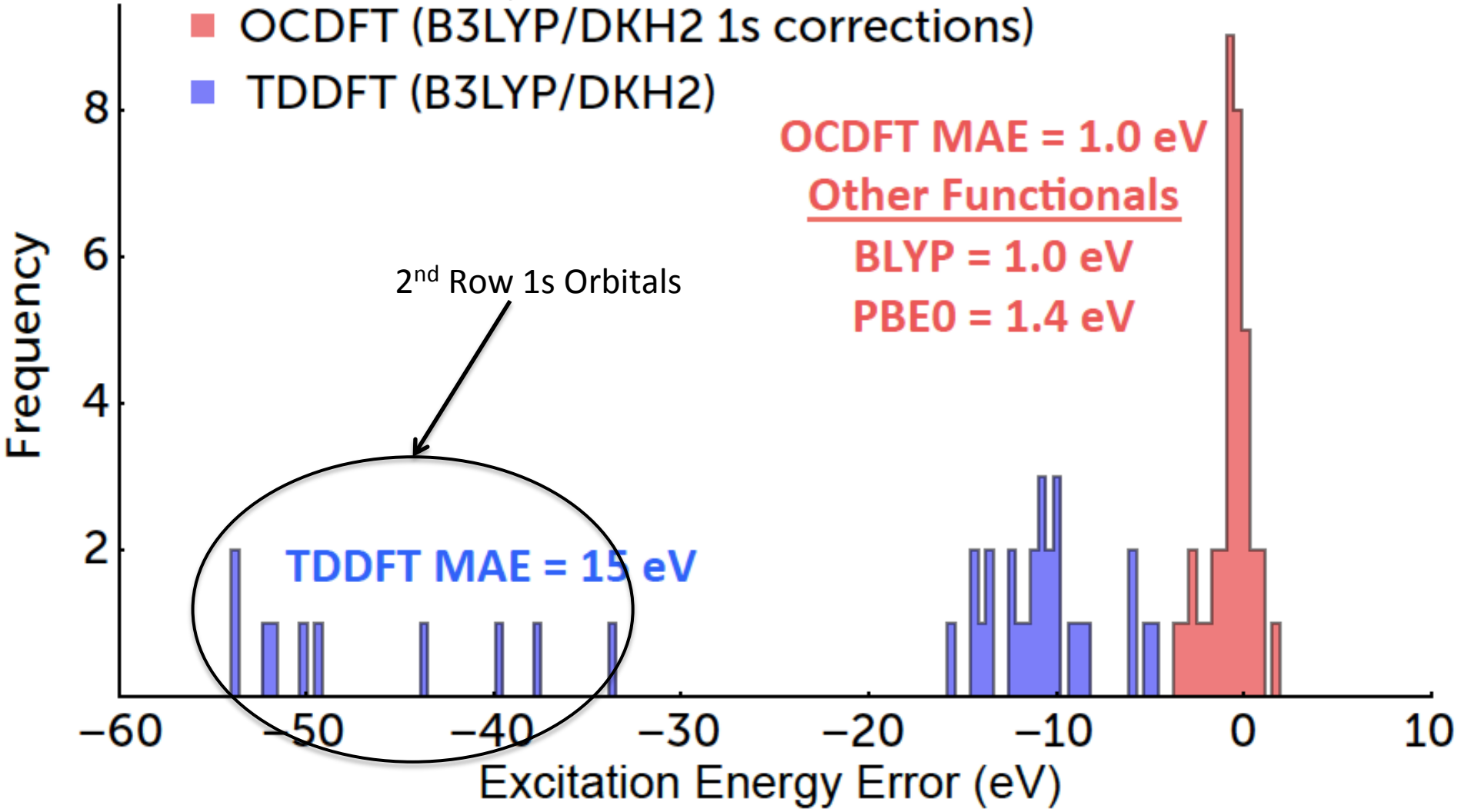

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Sensitivity to Orbital Overlap

- Comparing the sensitivity of OCDFT and TDDFT using Tozer Overlap Metric.[1]

$$\Lambda_{\mathrm{hp}} = \int |\varphi_h^{(n)}(r)||\varphi_p^{(n)}(r)|dr$$

1) Peach, M. J. G.; Benfield, P.; Helgaker, T.; Tozer, D. J., *J. Chem. Phys.* **2008**

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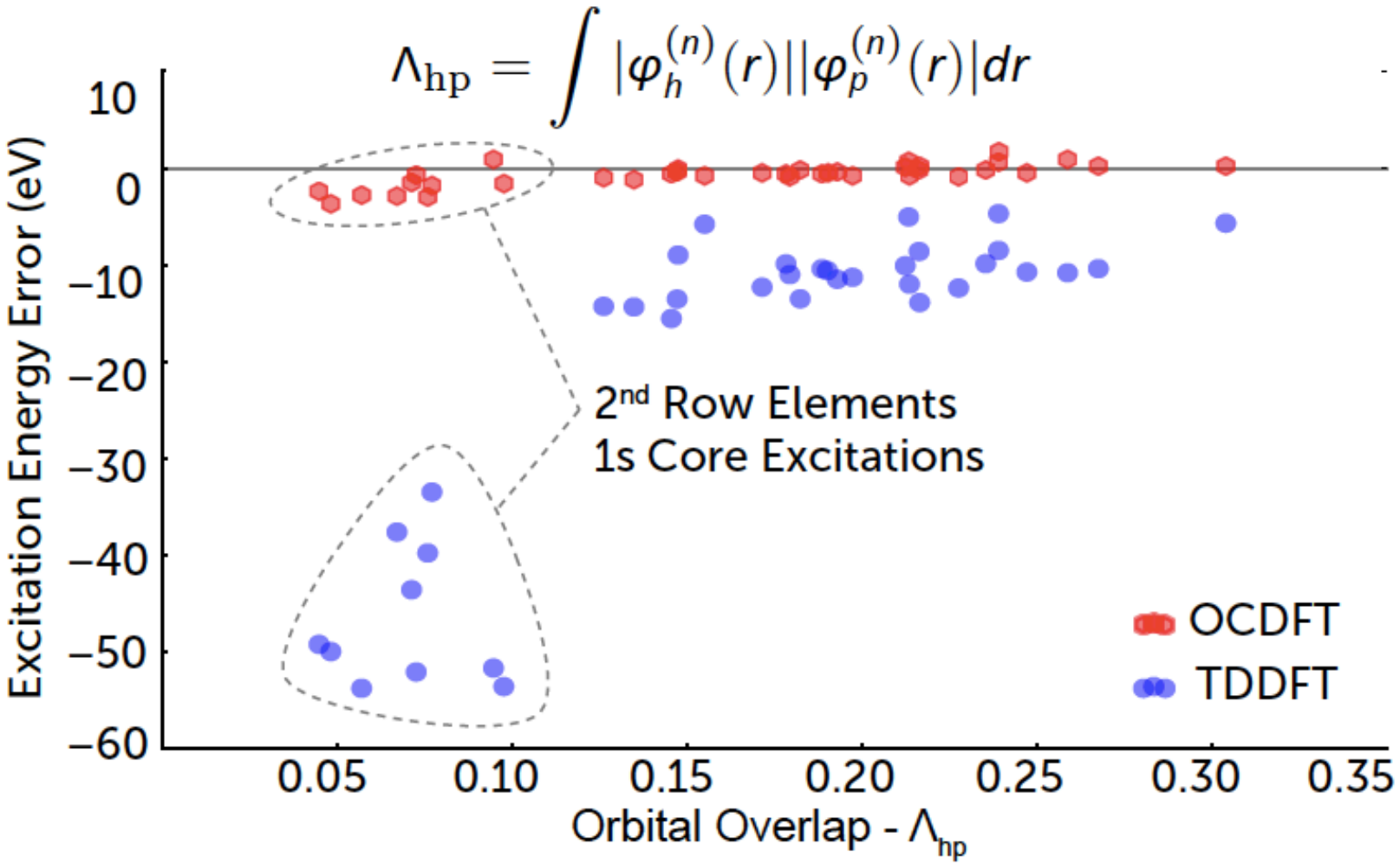

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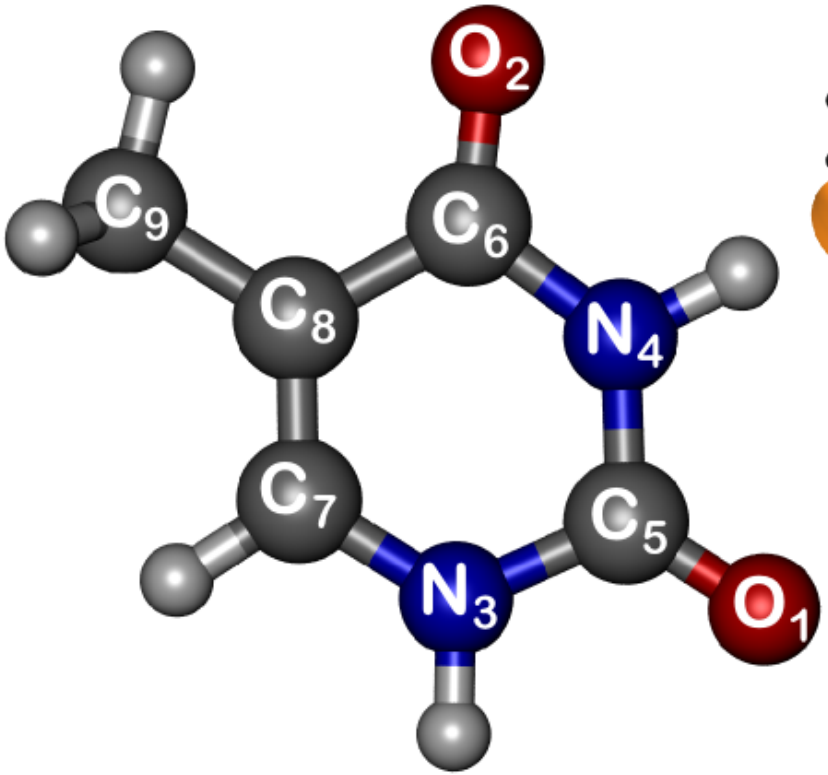
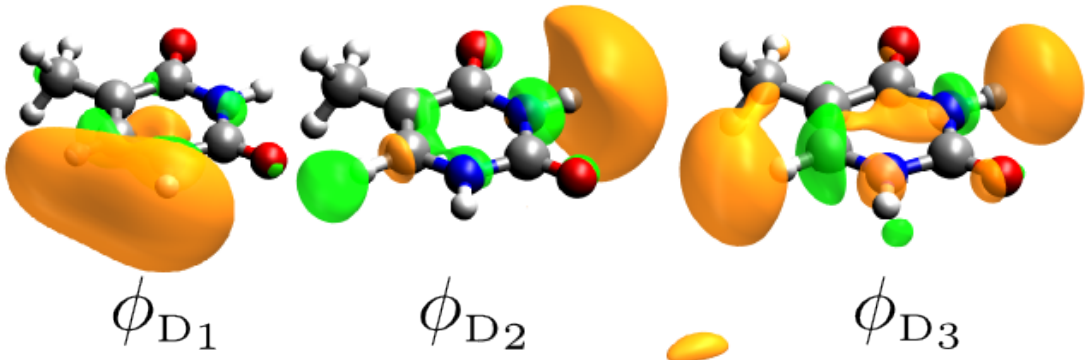
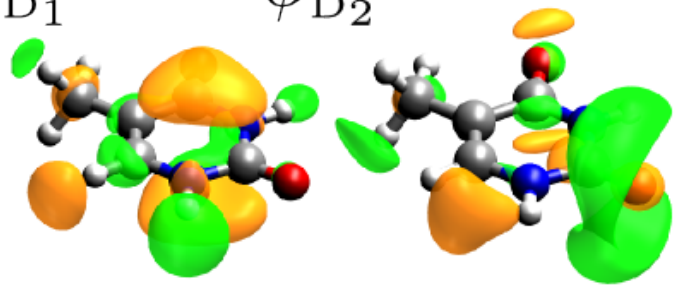
Application to Thymine



Diffuse Orbitals

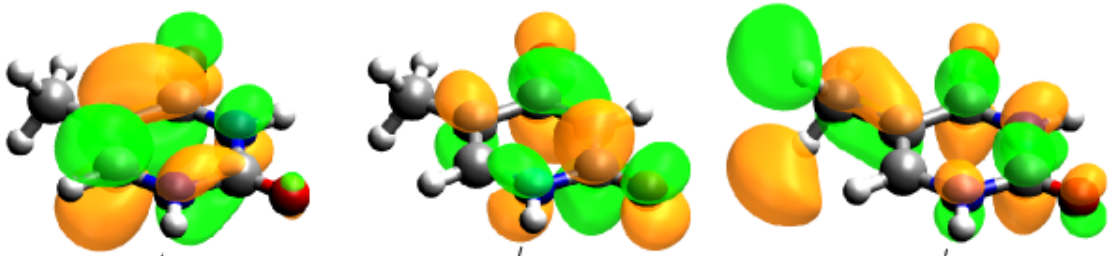


ϕ_{D1} ϕ_{D2} ϕ_{D3}



ϕ_{D4} ϕ_{D5}

Anti-Bonding Orbitals



$\phi_{\pi_1^*}$ $\phi_{\pi_2^*}$ $\phi_{\pi_3^*}$

Spectral Simulation Details

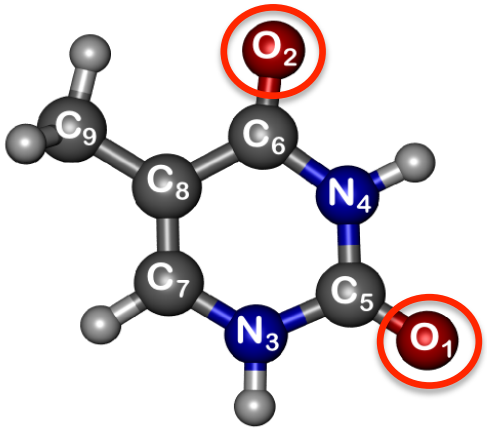
- Compute 10 excitations per hole for each carbon, nitrogen, and oxygen 1s orbital in thymine.
- Plot spectra using gaussians with FWHM of 0.1 eV - 0.4 eV in order to simulate natural spectroscopic broadening effects.
- Compare the OCDFT results with experiment and previously applied 2nd order algebraic diagrammatic construction [ADC(2)] methods
- Transition dipole moments are approximated using Kohn-Sham determinants and the position vector

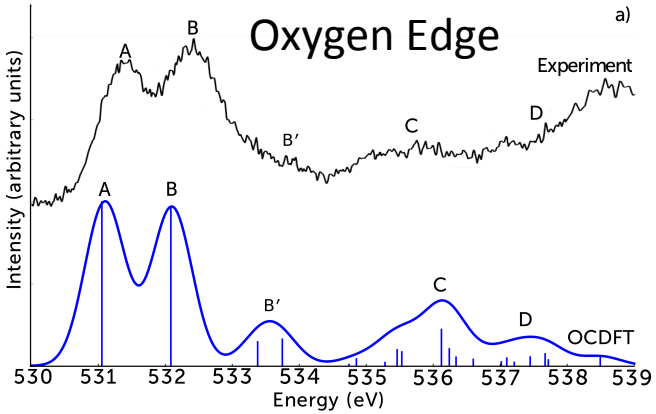
$$\mu_{fi} = \langle \Phi^{(f)} | \hat{r} | \Phi^{(i)} \rangle$$

- Using the approximate transition dipole moment we can now calculate an oscillator strength for each transition

$$f_{\mathrm{osc}} = \frac{2}{3} |\mu_{fi}|^2 \omega_{fi}$$

OCDFT Simulation of Thymine K-Edge





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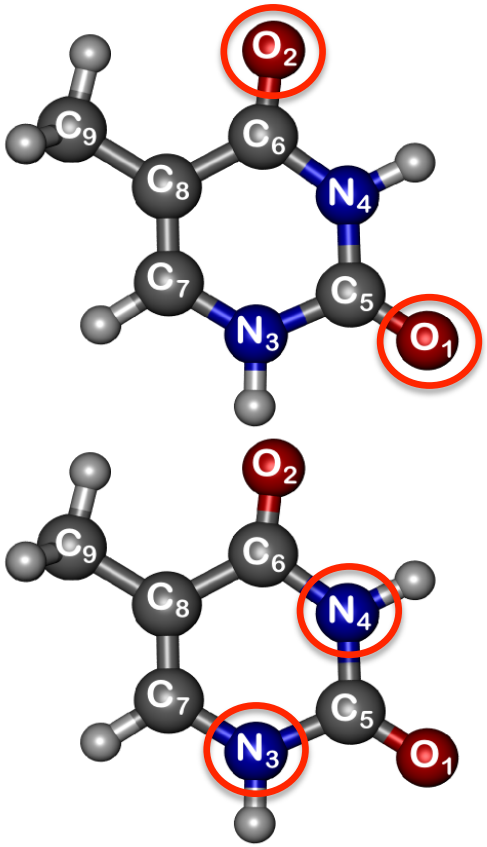

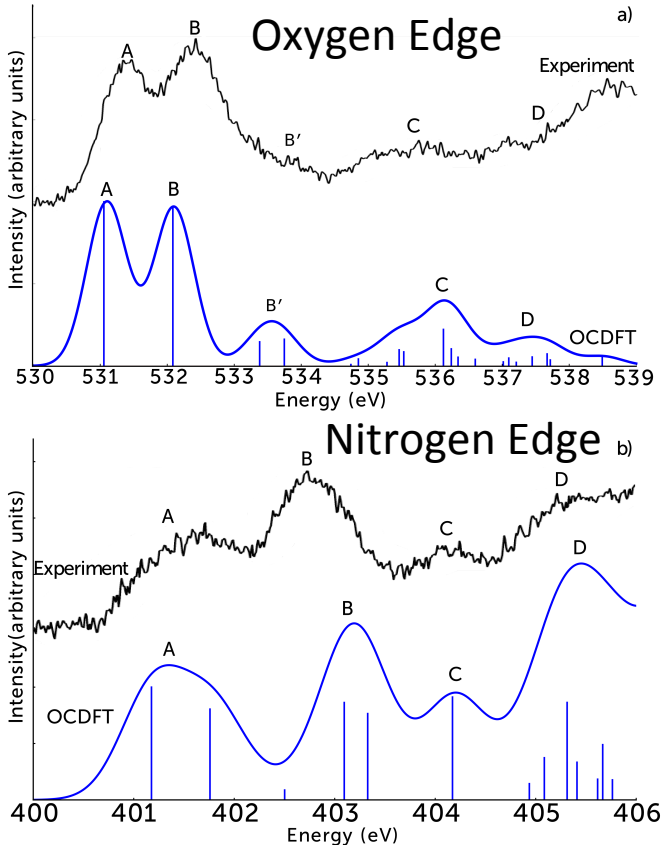

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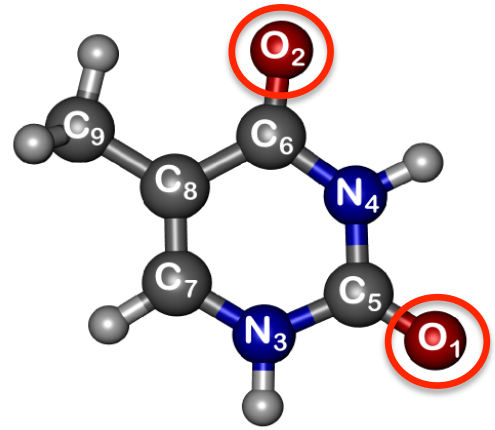

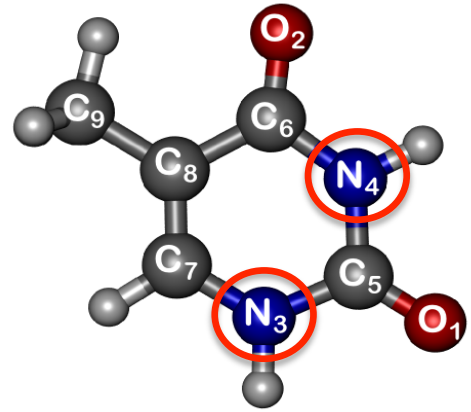

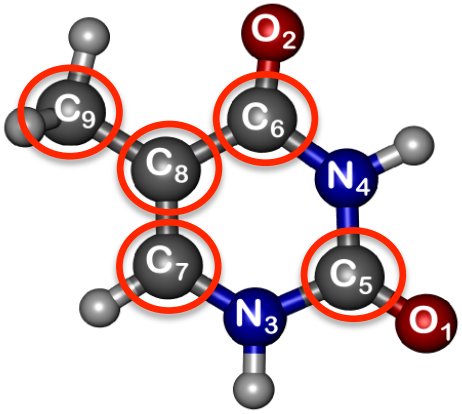

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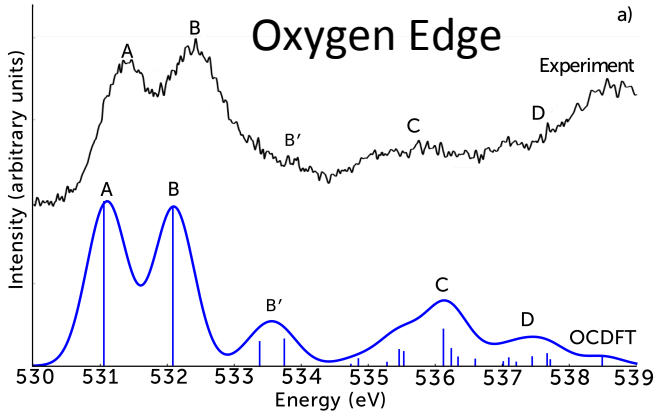
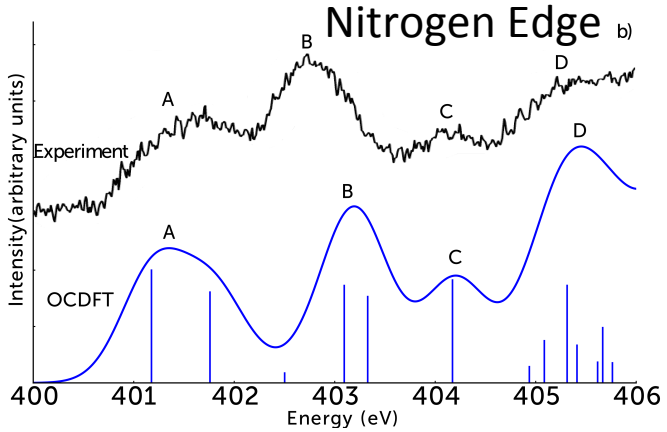
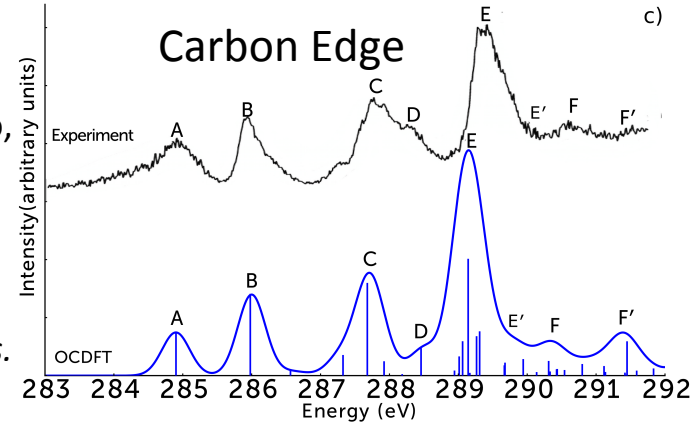
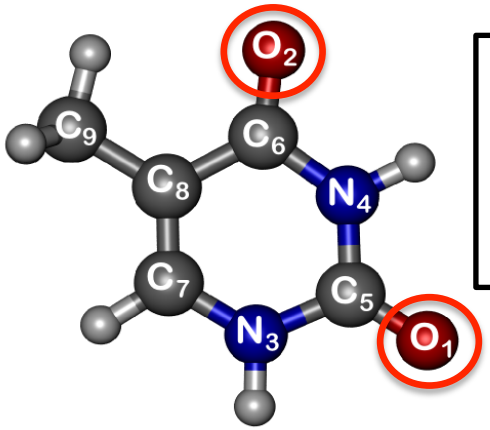
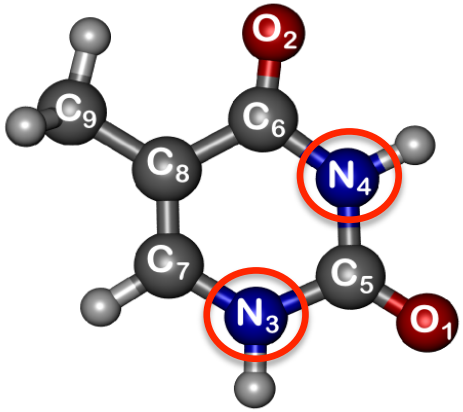


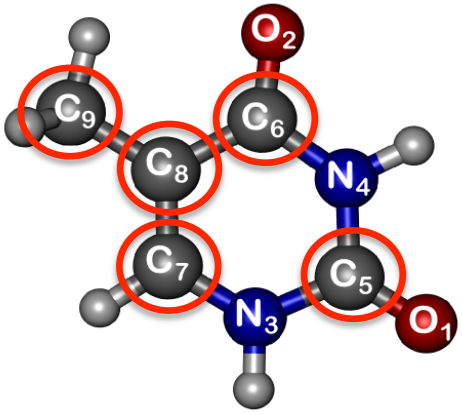




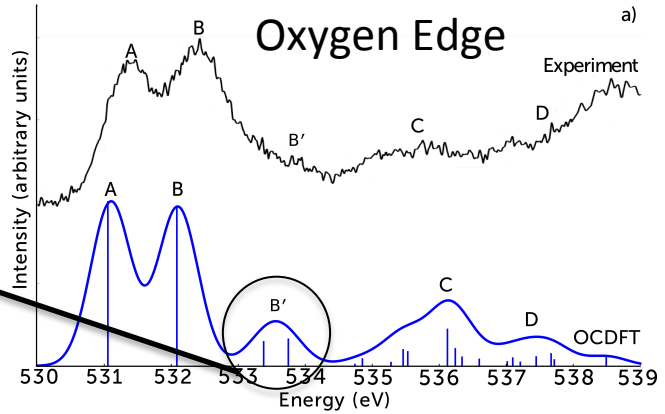
OCDFT Simulation of Thymine K-Edge

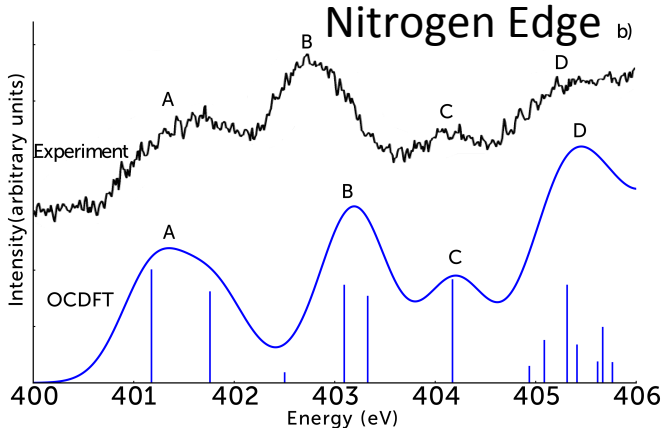


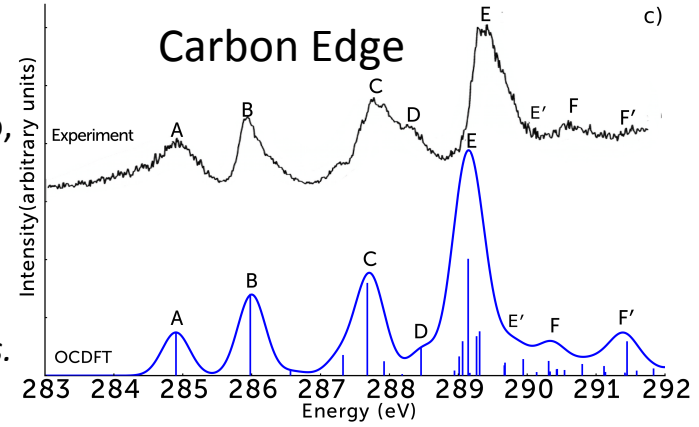




Shoulder Feature B' initially absent in ADC(2) spectrum.[1] Was confirmed by later CVS-ADC(2) study.[2]







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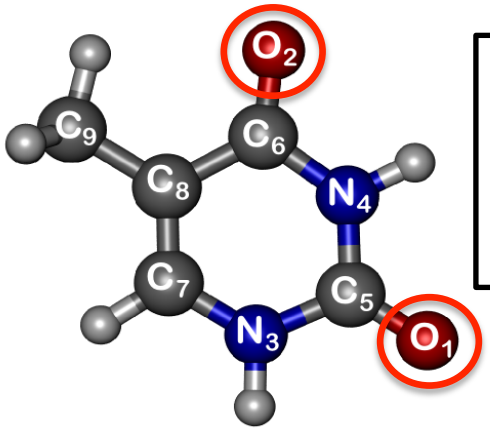

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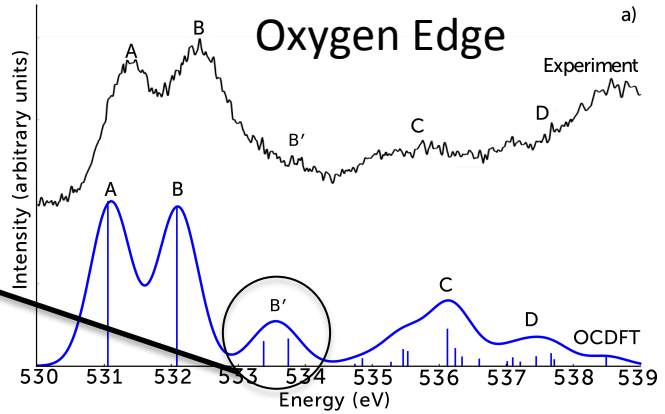
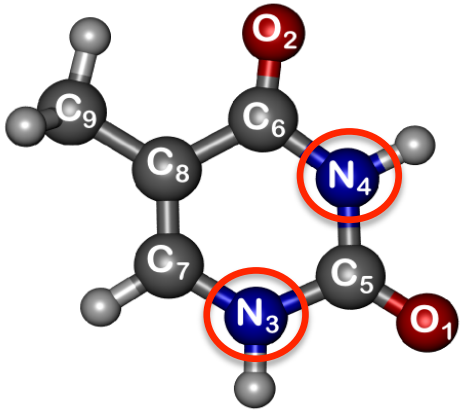
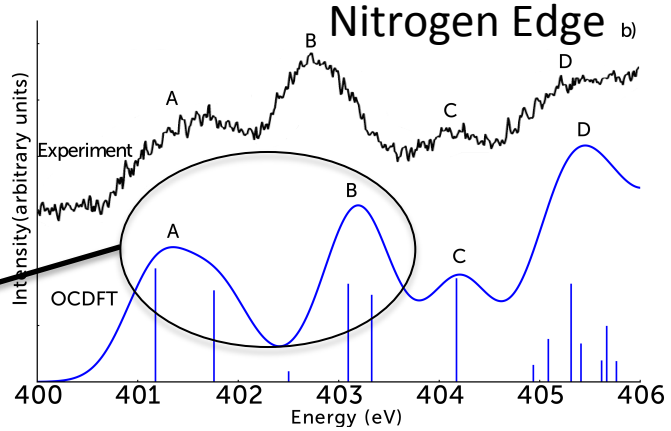
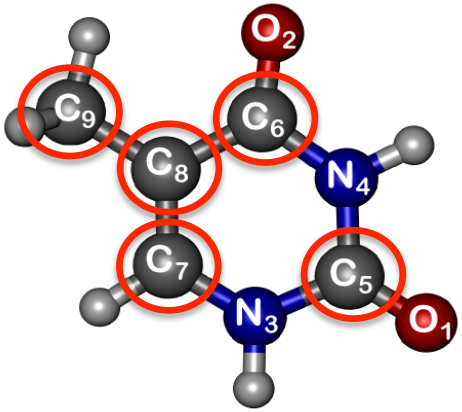




Peak Features A and B are unresolved in ADC(2) spectrum. Appear as single peak feature.





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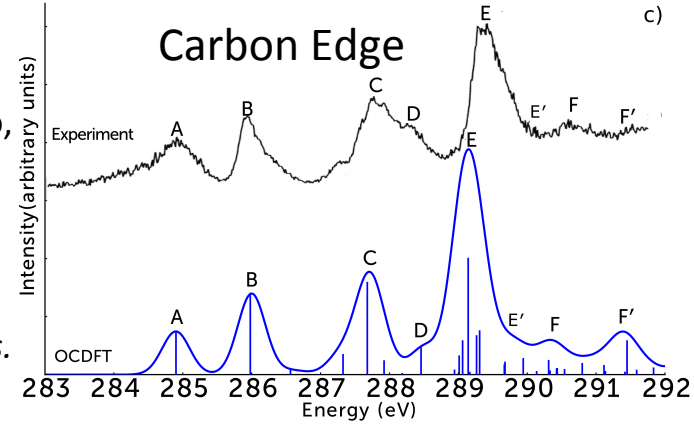
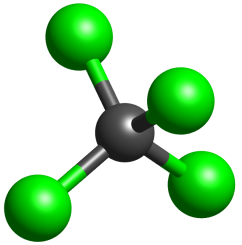
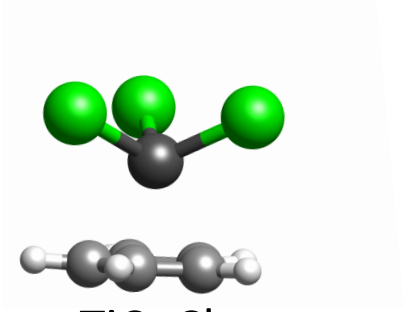


Application to Transition Metal Complexes

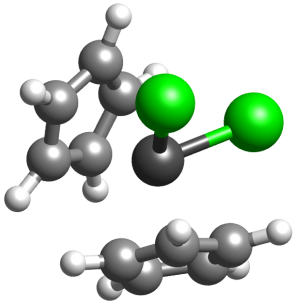
Ti K-Edge of Tetra coordinated Titanium Complexes



$TiCl_4$



$TiCpCl_3$



$TiCp_2Cl_2$

- Class of molecules used to study covalency in cyclopentadienyl (Cp) complexes relevant for use as anti-cancer drug.
- Full treatment of scalar relativistic effects will be handled by X2C Hamiltonian implemented as plugin in PSI4

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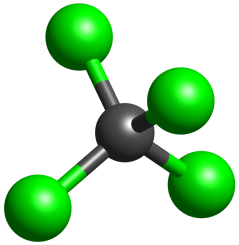

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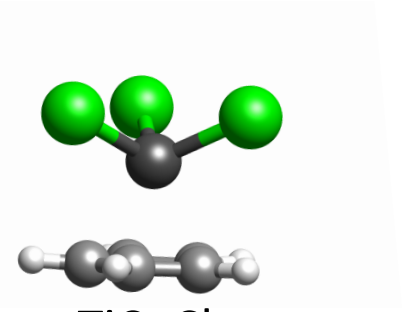

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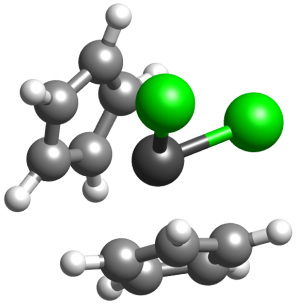

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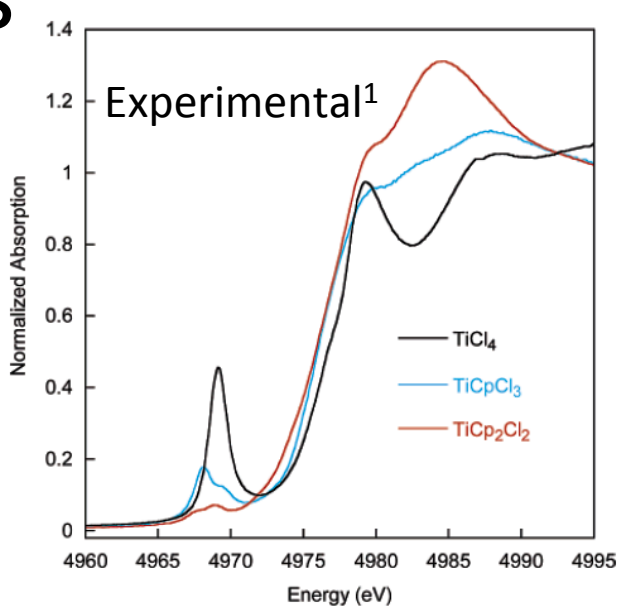

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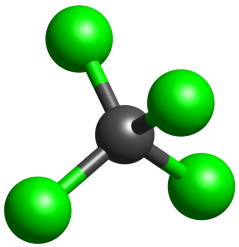

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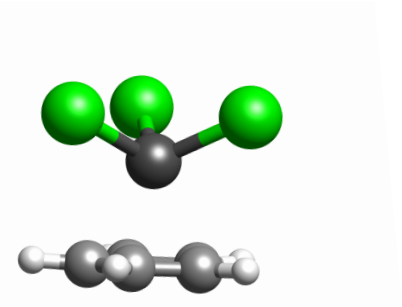

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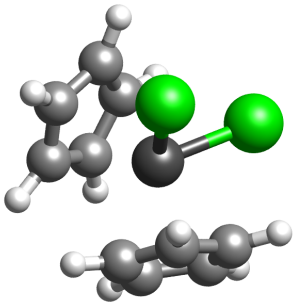

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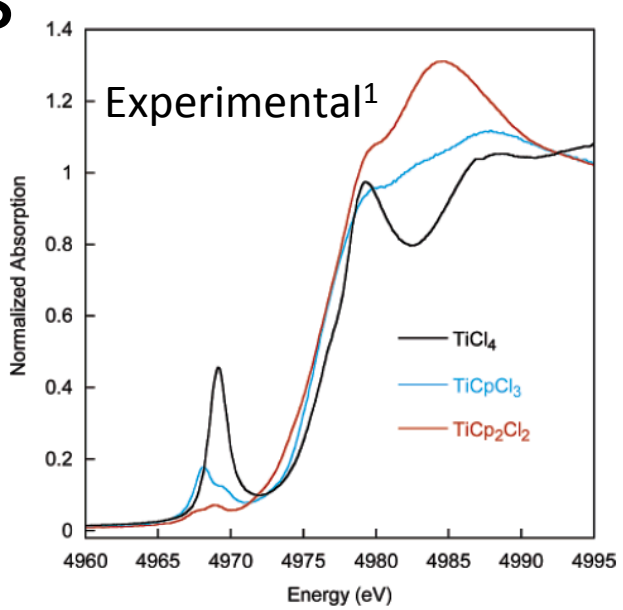

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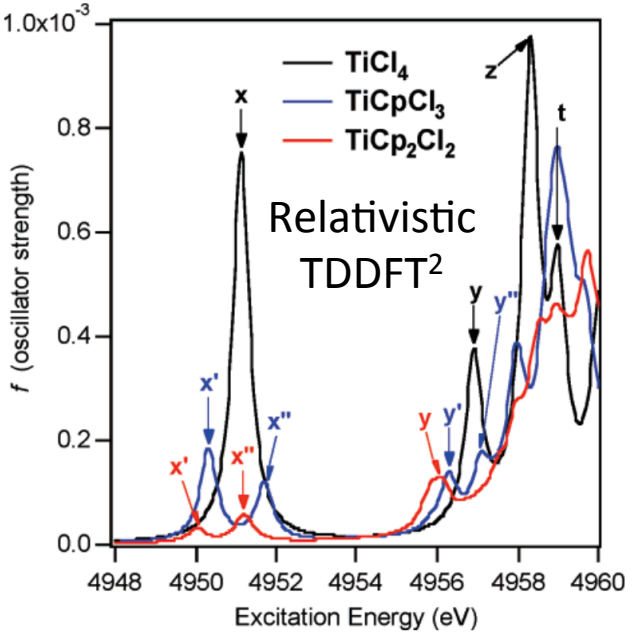

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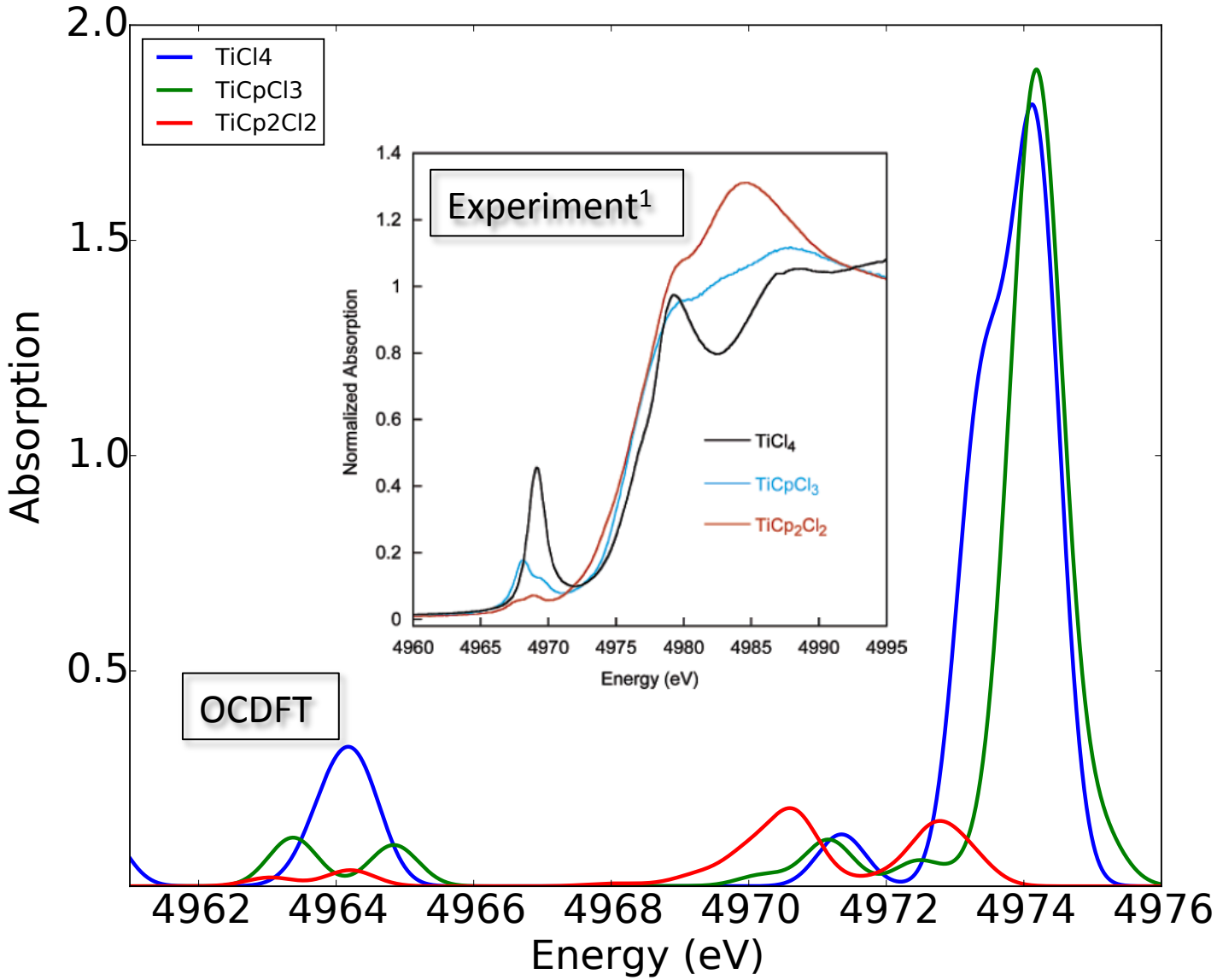
Comparison With Experimental Spectra



- Why are the peaks split for the Cp compounds? Maybe OCDFT Particle Orbitals can shed some insight?

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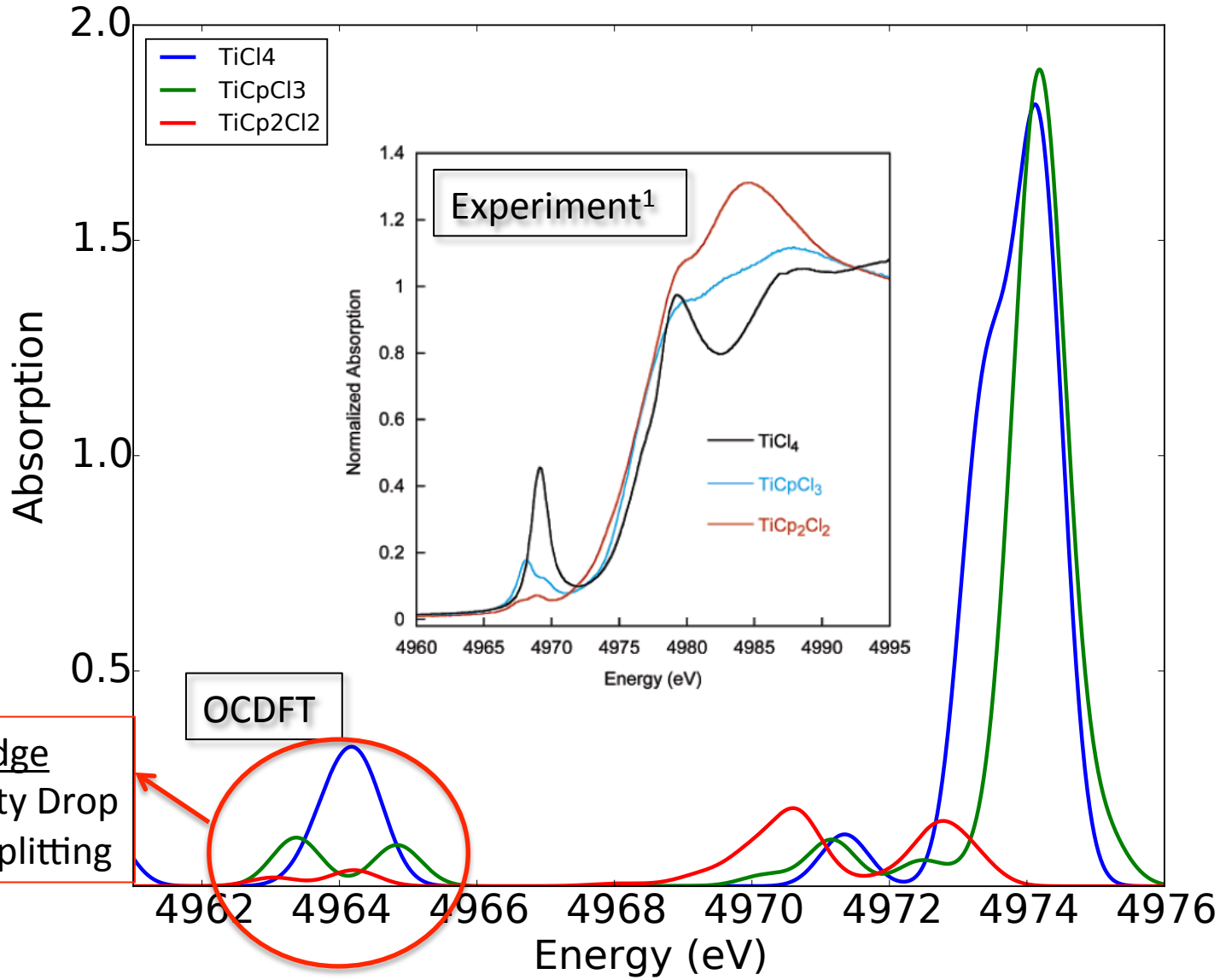

Pre-Edge
- Intensity Drop
- Peak Splitting

- Why are the peaks split for the Cp compounds? Maybe OCDFT Particle Orbitals can shed some insight?

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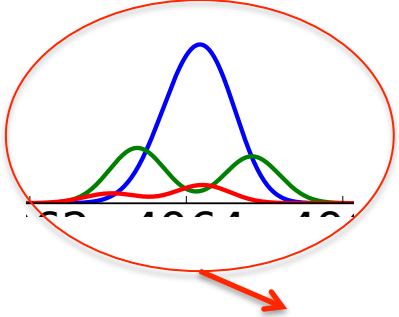


Pre-Edge Analysis

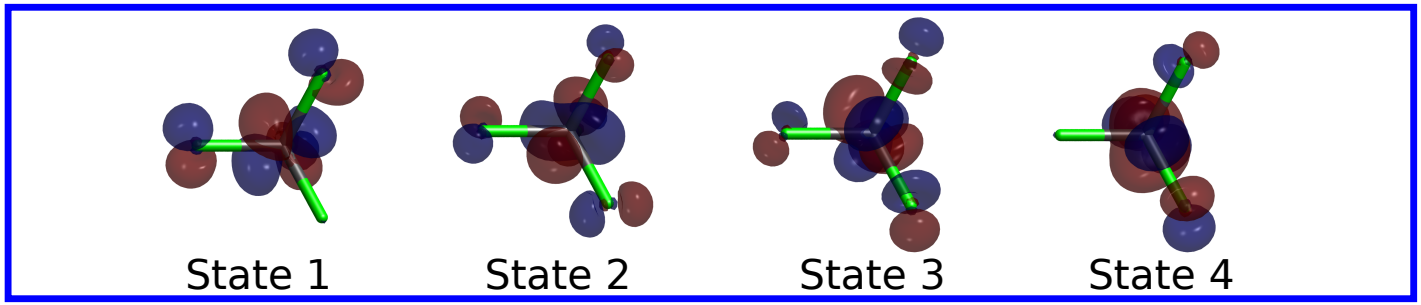
State	Transition Energy (eV)	Rel. Osc. Strength
	$TiCl_4$	
1	4963.85	0.0805
2	4963.53	0.0181
3	4964.38	0.1983
4	4964.03	0.1120

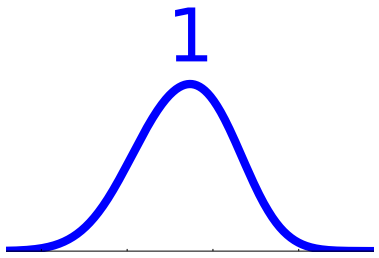
Particle Orbitals

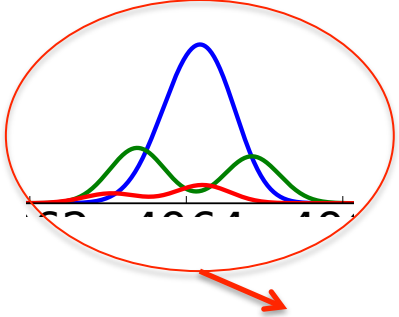
Pre-Edge

1

$TiCl_4$





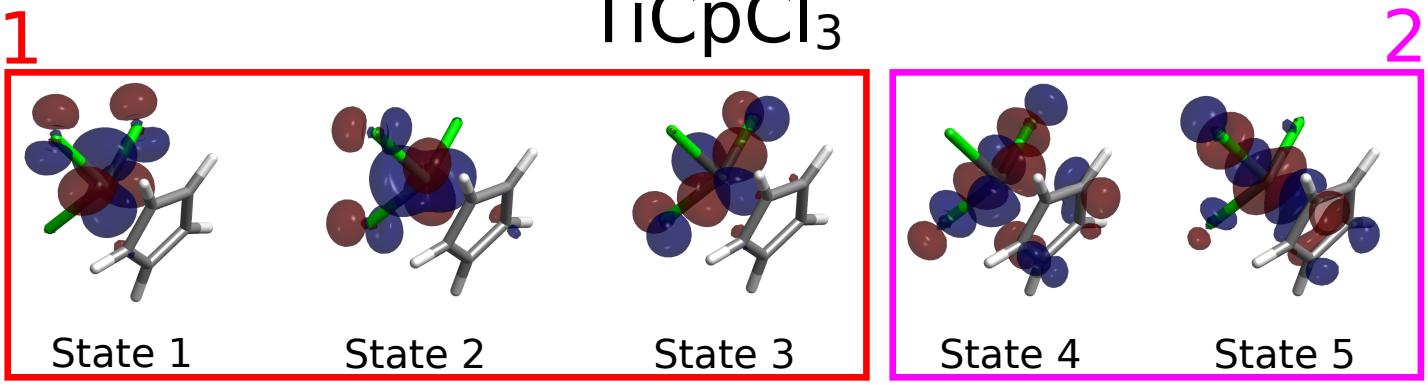


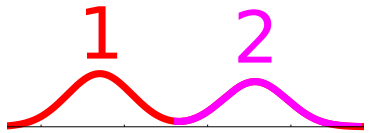
Pre-Edge Analysis

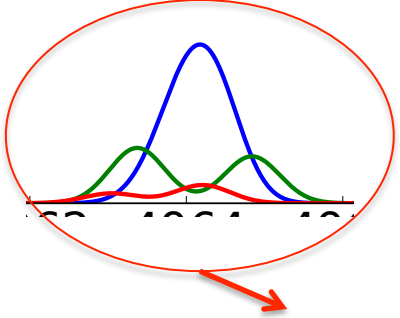
State	Transition Energy (eV)	Rel. Osc. Strength
	$TiCpCl_3$	
1	4963.31	0.0226
2	4963.38	0.0227
3	4963.45	0.0190
4	4964.80	0.0271
5	4964.88	0.0270

Particle Orbitals ***Pre-Edge***

$TiCpCl_3$





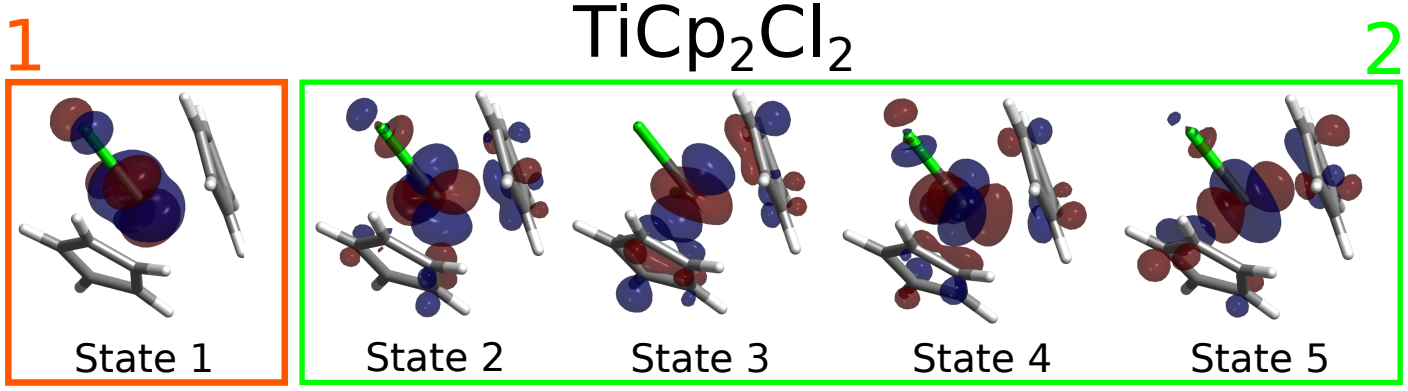


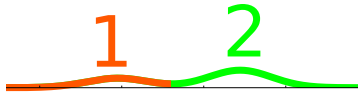
Pre-Edge Analysis

State	Transition Energy (eV)	Rel. Osc. Strength
	$TiCp_2Cl_2$	
1	4963.04	0.0114
2	4964.20	0.0079
3	4964.18	0.0012
4	4964.32	0.0003
5	4964.22	0.0116

Particle Orbitals ***Pre-Edge***

$TiCp_2Cl_2$





Conclusions

- Extended OCDFT to calculate multiple excited states in order to fully simulate NEXAS spectra.
- OCDFT has no significant dependence on the amount of Hartree-Fock exchange present in the functional
- Looked at excitations from first and second row elements and show that OCDFT is less sensitive to changes in orbital overlap.
- Calculated the NEXAS spectra of thymine in order to show that OCDFT is a useful tool for interpreting NEXAS spectra.
- Coupled OCDFT with X2C relativistic Hamiltonian in order to show that OCDFT can be effective at simulating NEXAS spectra of transition metal complexes.

Thank You

Evangelista Lab Members

Francesco Evangelista ← Advisor

Prakash Verma
Chenyang Li ← Post-Docs

Kevin Hannon
Jeff Schriber
Tianyuan Zhang ← Minions

NIH National Institutes of Health

EMORY

NSF GRADUATE RESEARCH FELLOWSHIP PROGRAM