

# Development and Applications of Orthogonality Constrained Density Functional Theory for the Accurate Simulation X-Ray Absorption Spectroscopy

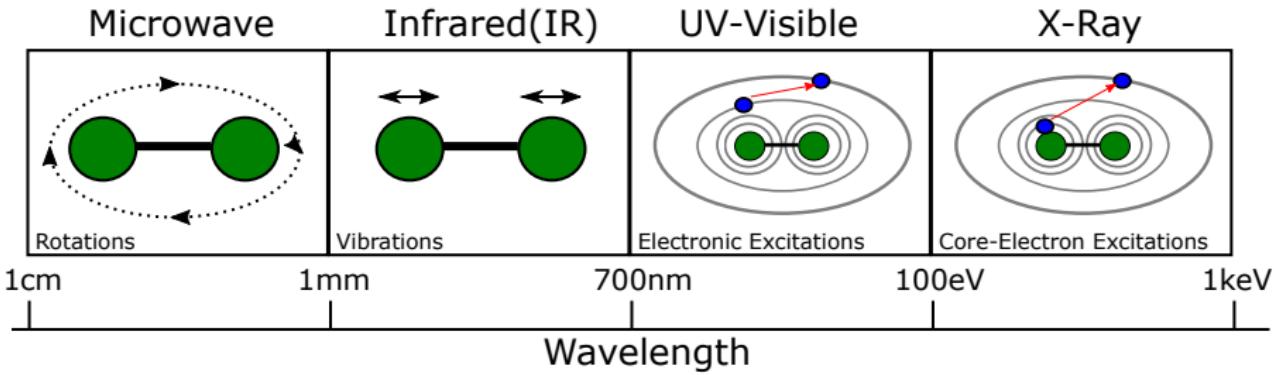
Wallace Derricotte

Dissertation Defense

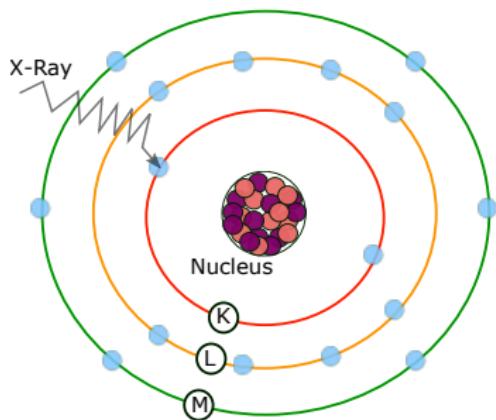
June 28th, 2017

# A Spectroscopy Primer

- Structural Characterization techniques, study interaction of a “probe” with a sample
- Knowledge of interaction gives information about structure
- Different probes have different interactions

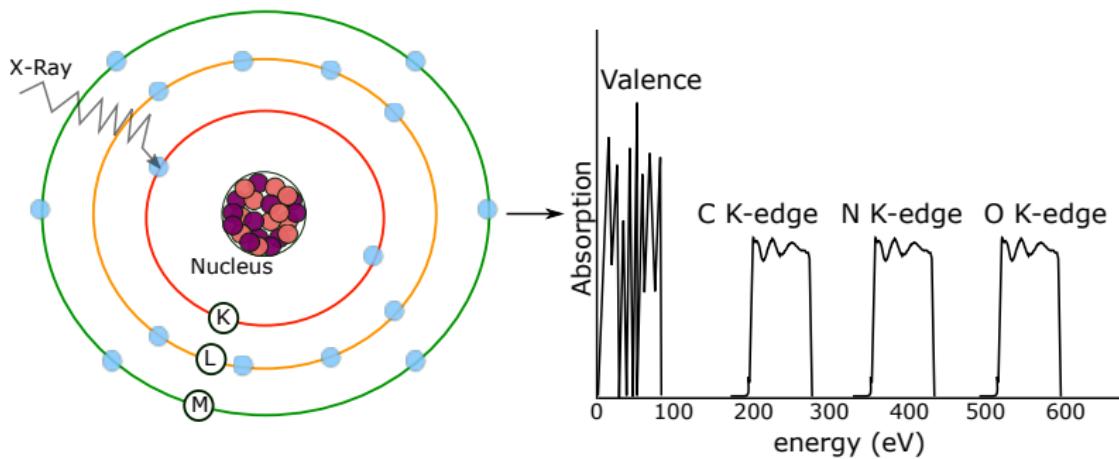


# X-ray Absorption Mechanism: Core-Excited States



- X-ray photons excite core electrons (i.e. 1s, 2s, 2p)
- Core orbitals are close to nuclei, experience strong Coulombic attraction

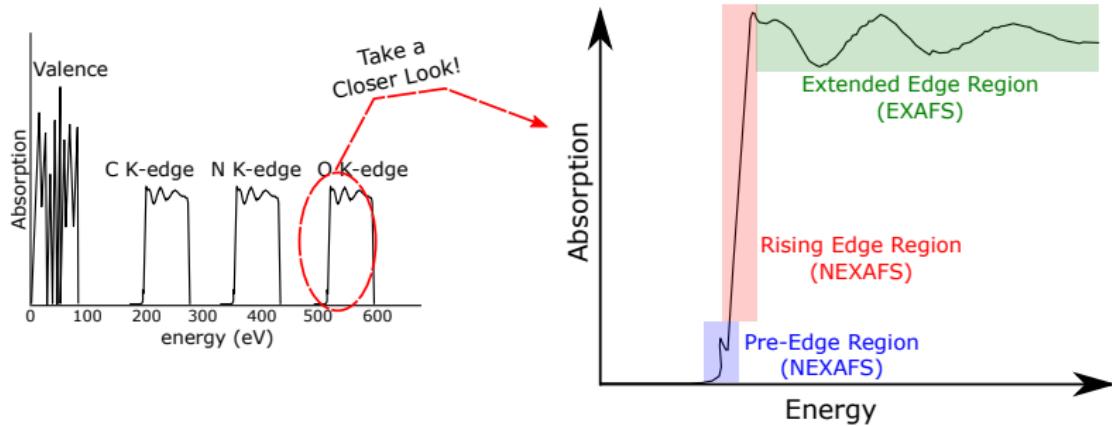
# X-ray Absorption Mechanism: Core-Excited States



- X-ray photons excite core electrons (i.e. 1s, 2s, 2p)
- Core orbitals are close to nuclei, experience strong Coulombic attraction
- Produces **element specific** edge jump in absorption spectrum
  - ▶ X-ray notation based on principal quantum number<sup>1</sup>(K=1, L=2, M=3)

<sup>1</sup>J. Stohr. *NEXAFS Spectroscopy*; Springer: 1992

# Fine Structure of the XAS Edge



- Edge has 3 distinct regions: Pre, Rising, and Extended Edges
- Near-edge X-ray absorption fine structure (NEXAFS) spectroscopy studies the pre and rising edge regions
- Extended-edge X-ray absorption fine structure (EXAFS) spectroscopy studies the extended edge region<sup>1</sup>

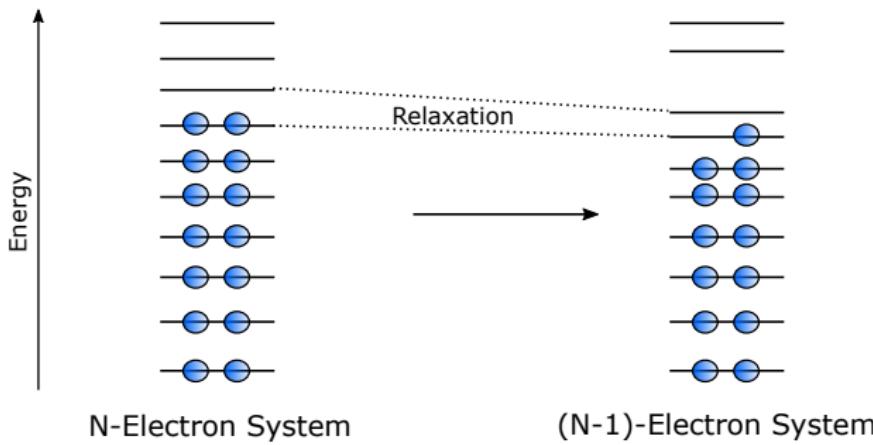
<sup>1</sup>B. K. Teo. EXAFS: Basic Principles and Data Analysis; Springer: 2012

# Computational Methods for Simulating NEXAFS

- Interpretation of NEXAFS requires knowledge of core-excitation energies, transition dipole moments, and orbital character of transition
- Wavefunction/Green's Function Methods
  - ▶ Linear Response Coupled Cluster (LR-CC)
  - ▶ Algebraic Diagrammatic Construction (ADC)
  - ▶ SOS-CIS(D)
- Density Functional Theory Methods
  - ▶ Linear Response Time-Dependent DFT (TDDFT)
  - ▶ Real-Time TDDFT
- Hartree–Fock (HF) Based Approaches
  - ▶ HF Static Exchange Method (HF-STEX)
  - ▶ Maximum Overlap  $\Delta$ SCF
- All methods face unique challenges when calculating core excited states

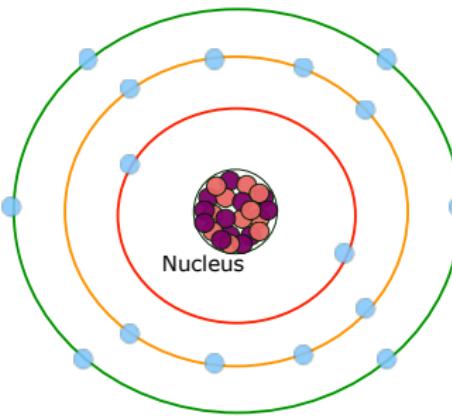
# Theoretical Challenges: Orbital Relaxation

- Orbital relaxation effects can be understood formally as the change in orbital energies when changing the number of electrons



- Remaining orbitals are drawn closer to the nucleus which becomes more effectively screened

# Orbital Relaxation Effects in Core-Excited States

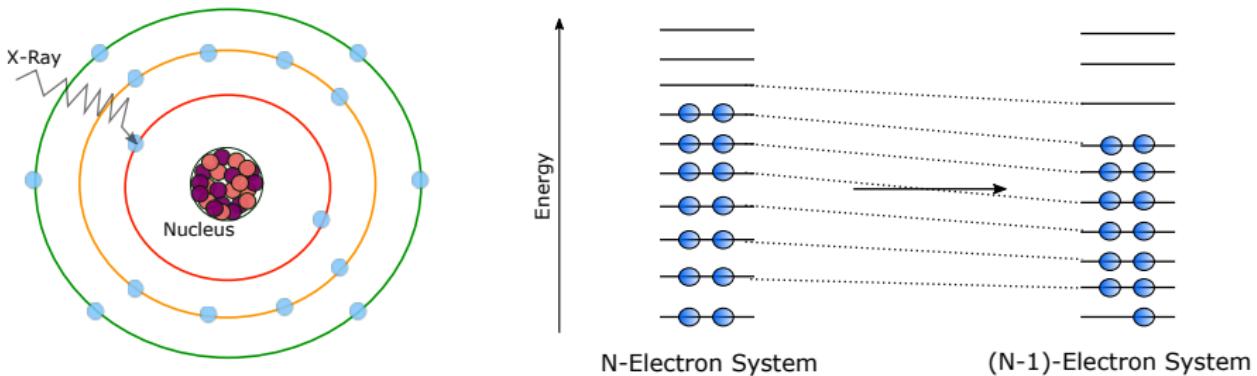


- Effective nuclear charge ( $Z_{\text{eff}}$ ) on any electron can be approximated as:

$$Z_{\text{eff}} = Z - \sigma \quad (1)$$

- where  $Z$  is the number of protons and  $\sigma$  is the average number of electrons b/w the nucleus and the electron in question

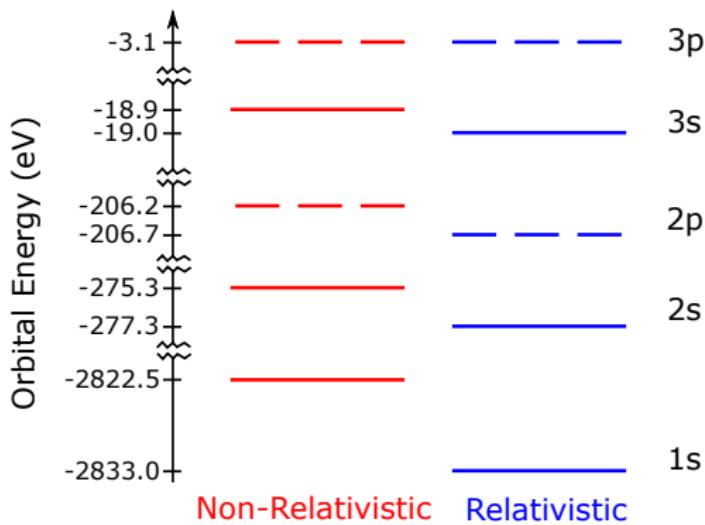
# Orbital Relaxation Effects in Core-Excited States



- Generation of a core-hole causes a decrease in the shielding of the nuclei
- Causes significant rearrangement in all higher lying orbitals, known as **orbital relaxation**
- It was shown that for a N atom, this effect can be on the order of 12-15 eV<sup>1</sup>

<sup>1</sup>B. N. Plakhutin; E. V. Gorelik; N. N. Breslavskaya. *J. Chem. Phys.* 2006

# Theoretical Challenges: Relativistic Effects



Orbital energies of  $\text{Cl}^-$  from non-relativistic and scalar relativistic Hartree–Fock calculations.

- Core orbitals experience large **relativistic** contraction while the valence orbitals remain relatively unaffected
- Results in increase in core-excitation energy

# Theoretical Challenges: Relativistic Effects

Table 1: Non-relativistic (NR) and relativistic (R) energies (in eV) of the lowest lying core orbital and lowest unoccupied molecular orbital (LUMO) of water ( $\text{H}_2\text{O}$ ) and silane ( $\text{SiH}_4$ ) molecules calculated using spin-unrestricted Hartree–Fock (UHF) with the 3-21G basis set. Scalar relativistic effects are included by use of the 2<sup>nd</sup> order Douglas-Kroll-Hess Hamiltonian.<sup>1</sup> All calculations were performed using the ORCA software package.

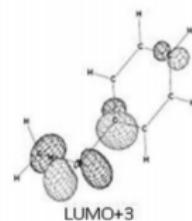
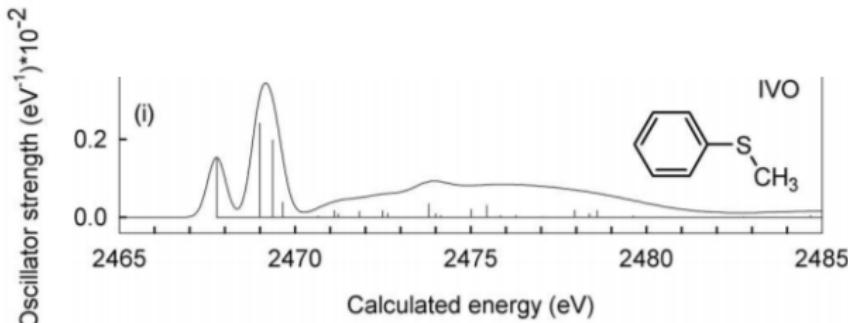
$\text{H}_2\text{O}$		$\text{SiH}_4$		
	O 1s	LUMO	Si 1s	LUMO
NR-UHF	−555.88	7.17	−1858.20	5.02
R-UHF	−556.34	7.16	−1863.04	5.03

- Effect is more pronounced in heavier elements
- Small but non-negligible effect on light elements

<sup>1</sup>M. Reiher. *Theor. Chem. Acc.*. 2006

# Theoretical Challenges: Assigning Excited States

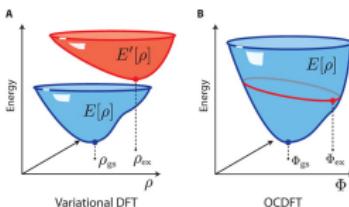
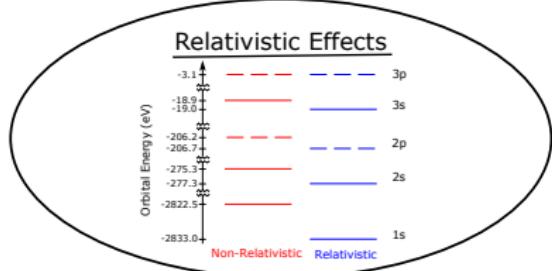
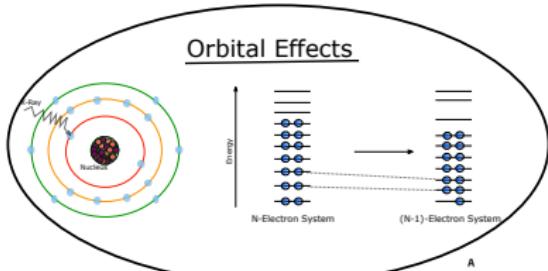
- Excited states are often assigned based on MO plots relative to the ground state



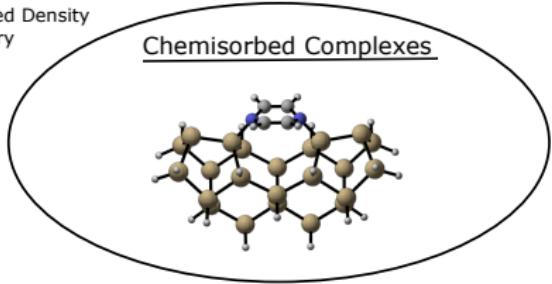
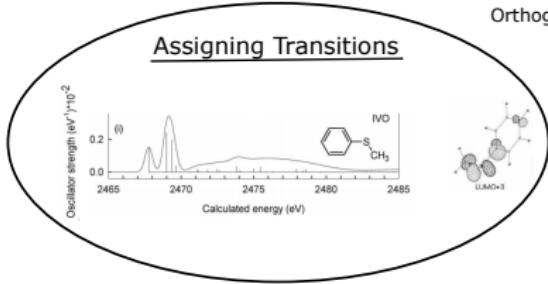
- LUMO+3 for methylsulfanyl benzene above was assigned as  $\pi^*(\text{C}=\text{C})$ ,<sup>1</sup> but other contributions are clearly present
- Two issues with this type of assignment
  - Assignments based on MO plots are potentially ambiguous
  - Approach is not systematic/reproducible

<sup>1</sup>S. Behyan; Y. Hu; S. G. Urquhart. *J. Chem. Phys.* 2013

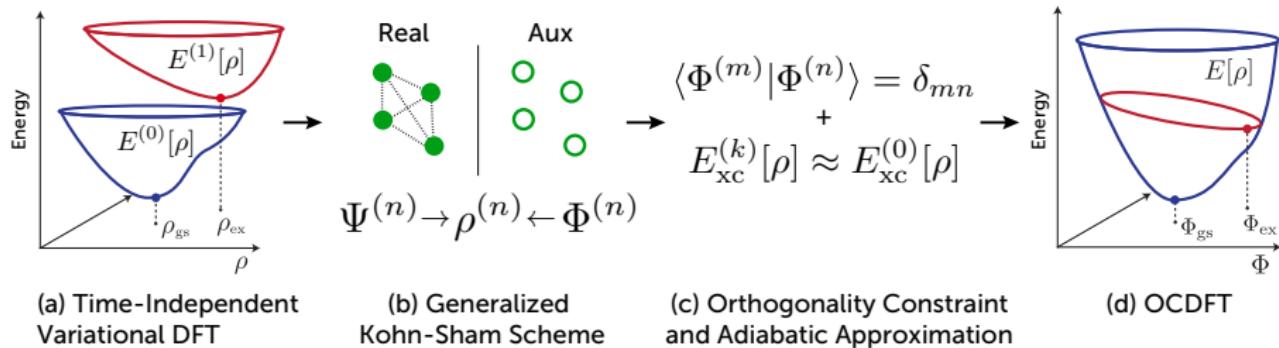
# Overview of Dissertation Work



Orthogonality Constrained Density Functional Theory



# Orthogonality Constrained Density Functional Theory<sup>1</sup>

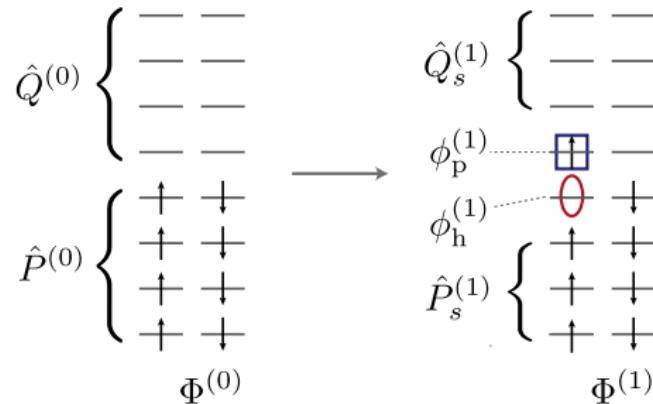


- Variational time-independent (TI) formulation of density functional theory (DFT)
- This choice of constraint prevents **variational collapse** of the excited state SCF
- OCDFT excited state functional can be written as:

$$E_{\text{OCDFT}}^{(n)}[\{\phi_i^{(n)}\}] = -\frac{1}{2} \sum_i^{\text{occ}} \langle \phi_i^{(n)} | \nabla^2 | \phi_i^{(n)} \rangle + \int d\mathbf{r} v(\mathbf{r}) \rho^{(n)}(\mathbf{r}) + J[\rho^{(n)}] + E_{\text{xc}}^{(0)}[\rho^{(n)}]. \quad (2)$$

<sup>1</sup>F. A. Evangelista; P. Shushkov; and J. C. Tully. *J. Phys. Chem. A*. 2013

# OCDFT: Minimal Orthogonality Conditions



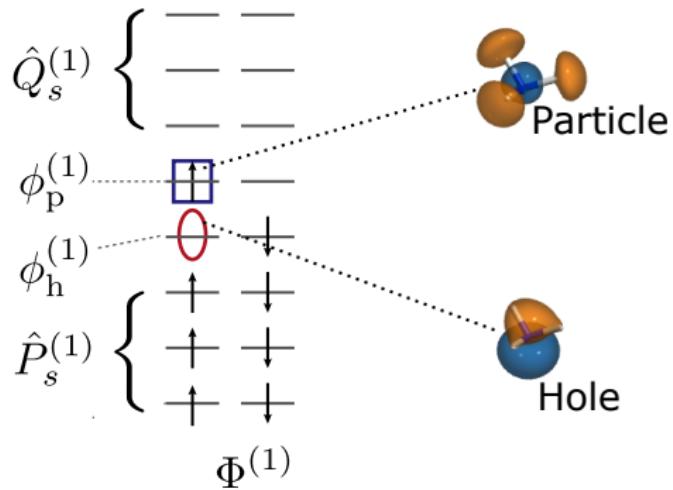
- Enforcing orthogonality introduces a *hole* ( $\phi_h^{(1)}$ ) and *particle* ( $\phi_p^{(1)}$ ) orbital that must satisfy the following:

$$\hat{Q}^{(0)} \phi_h^{(1)} = 0, \quad (3)$$

$$\hat{P}^{(0)} \phi_p^{(1)} = 0, \quad (4)$$

- In quasiparticle formalism,  $\phi_h^{(1)}$  and  $\phi_p^{(1)}$  define the single excitation

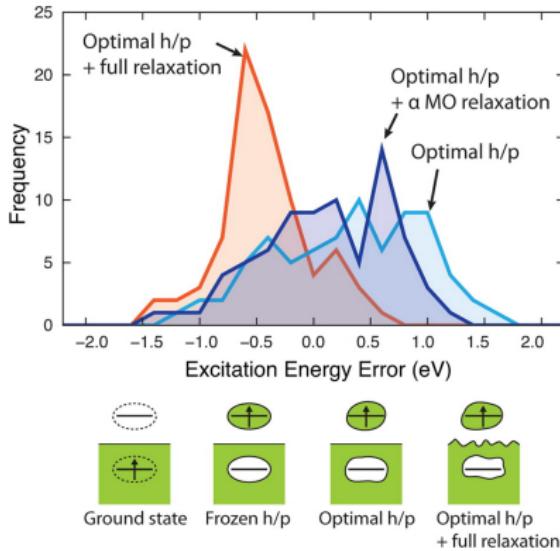
# OCDFT: Hole and Particle Orbitals in Practice



Particle orbitals for first excited state in  $\text{NH}_3$ . Calculated using OCDFT at B3LYP/3-21G level of theory

- Visual representation of each single excited state
- $\phi_h^{(1)}$  and  $\phi_p^{(1)}$  are variationally optimized for the excited state

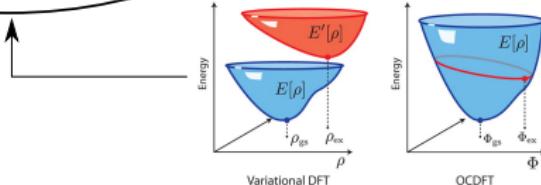
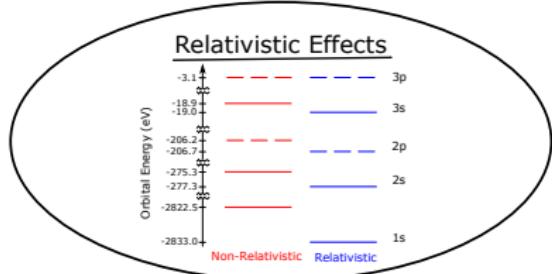
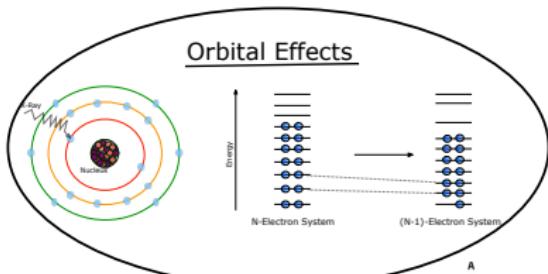
# Treatment of Orbital Relaxation in OCDFT



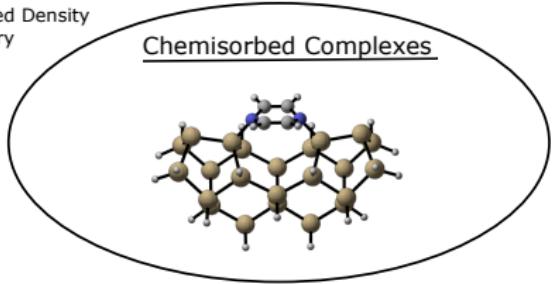
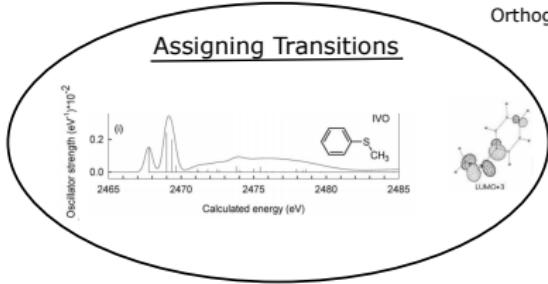
- Original tests on valence excitation showed full inclusion of relaxation effects yielded best results<sup>1</sup>
- If the theory is extended to core excitation we can benefit from full inclusion of orbital relaxation

<sup>1</sup>F. A. Evangelista; P. Shushkov; and J. C. Tully. *J. Phys. Chem. A.* 2013

# Developing OCDFT For Core-Excited States

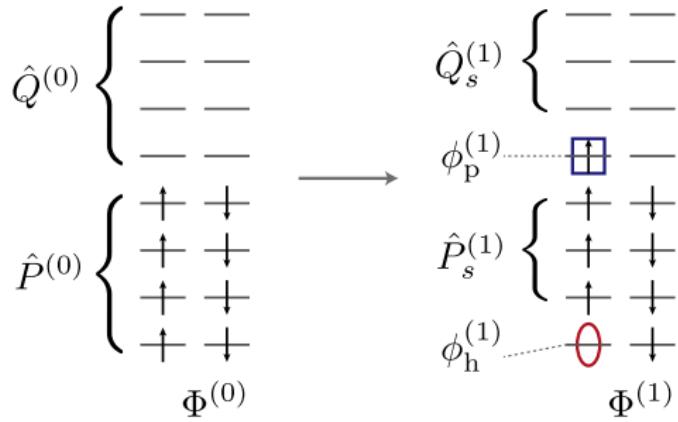


Orthogonality Constrained Density Functional Theory



# Extension of OCDFT For NEXAFS Spectral Simulation

- Must introduce two new features to OCDFT to calculate NEXAFS spectra
  - Previous implementation starts from *highest lying* hole orbital (highest hole eigenvalue) however for core excitations we need to select the *lowest lying* hole orbital (lowest hole eigenvalue)
  - Algorithm must be generalized to multiple excited states



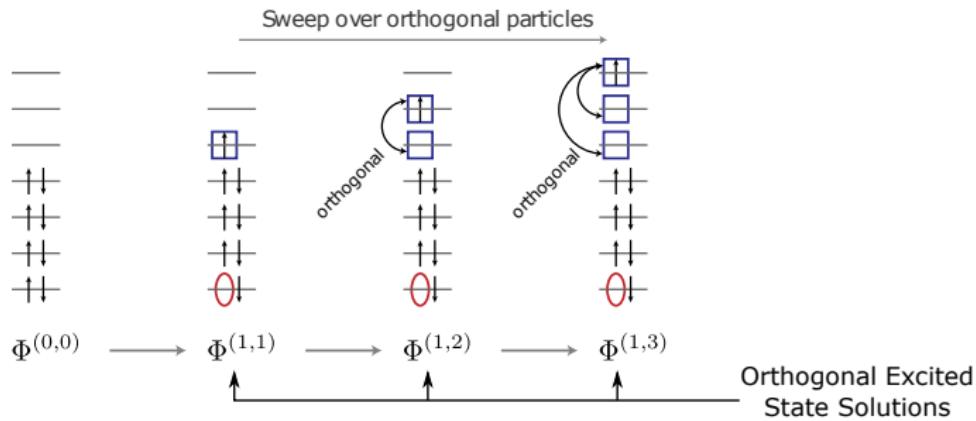
# Extension of OCDFT For NEXAFS Spectral Simulation

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↑↑  
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$\Phi^{(0,0)}$   
↑ Ground State Determinant

- First, perform a ground state DFT calculation to obtain the ground state determinant  $\Phi^{(0,0)}$
- Utilizing notation  $\Phi^{(i,a)}$  where  $i$  and  $a$  are hole and particle indices respectively

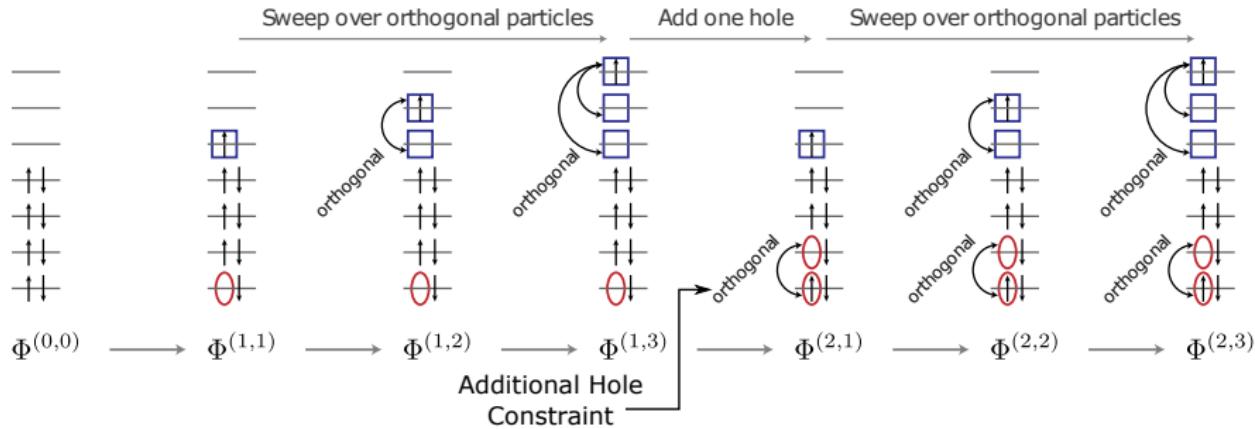
# Extension of OCDFT For NEXAFS Spectral Simulation



- Perform a sweep of  $n_u$  particle orbitals to produce a series of core-excited solutions:  $\Phi^{(1,1)}, \Phi^{(1,2)}, \dots, \Phi^{(1,n_u)}$ .
- Characterized by particle orbitals that produce an orthonormal set:

$$\langle \phi_p^{(1,a)} | \phi_p^{(1,b)} \rangle = \delta_{ab}, \quad \forall a, b \leq n_u. \quad (5)$$

# Extension of OCDFT For NEXAFS Spectral Simulation

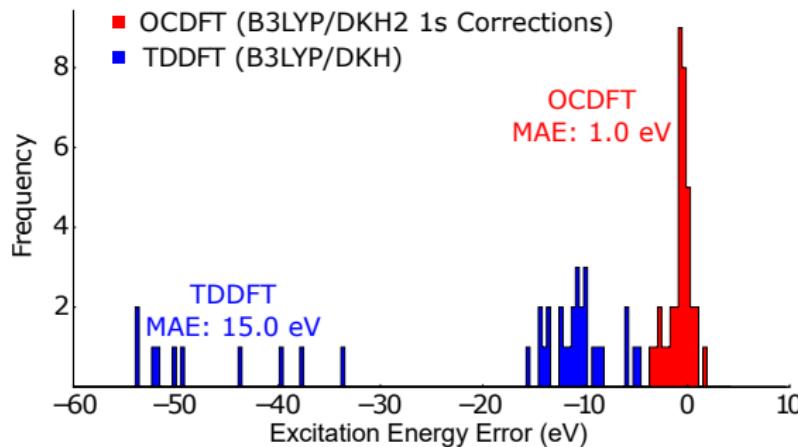


- Increase core index by one and sweep through another series of core-excited solutions:  $\Phi^{(2,1)}, \Phi^{(2,2)}, \dots, \Phi^{(2,n_u)}$ .
- Where an additional constraint is added to the hole orbital to be orthogonal to the hole orbital of the first sweep:

$$\langle \phi_h^{(1,1)} | \phi_h^{(2,a)} \rangle = 0, \quad \forall a \leq n_u. \quad (6)$$

# Core-Excited State Benchmark Test Set

- Benchmark test set consists of 40 core-excitations from 13 different molecules



- Max Errors:
  - OCDFT: -3.7 eV
  - TDDFT: -53.6 eV
- MAE of Other Methods:
  - EOM-CCSD: 0.9 eV
  - SOS-CIS(D): 1.2 eV

## Full NEXAFS Spectral Simulation: Thymine

- Transition dipole moments (TDMs) are approximated using the Kohn–Sham determinants as:

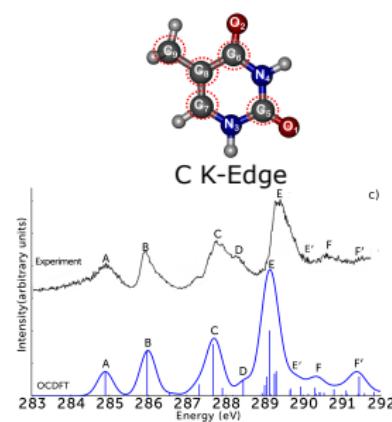
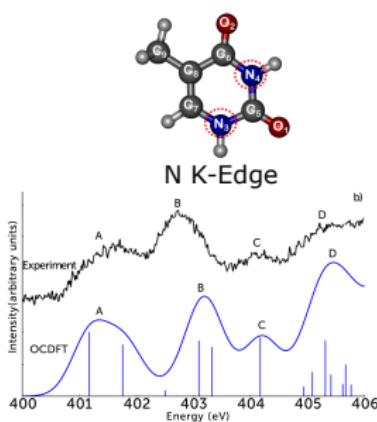
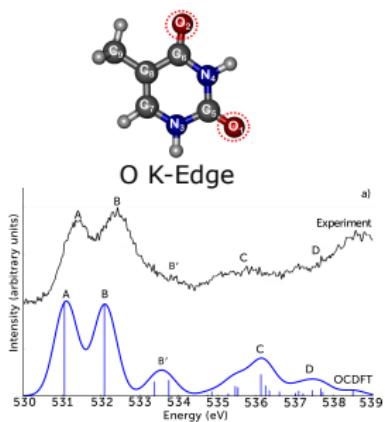
$$\mu_{n0} = \langle \Phi^{(n)} | \hat{\mathbf{r}} | \Phi^{(0)} \rangle \quad (7)$$

- Using the approximate TDMs we can compute an oscillator strength for each transition

$$f_{\text{osc}} = \frac{2}{3} |\mu_{n0}|^2 \omega_n \quad (8)$$

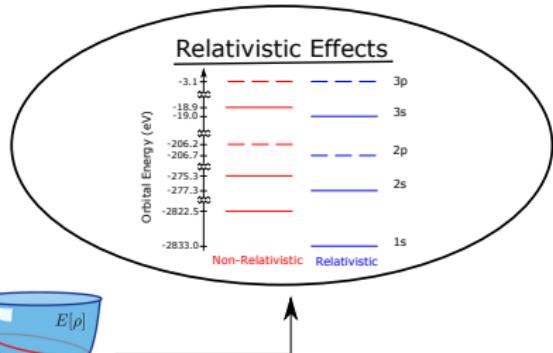
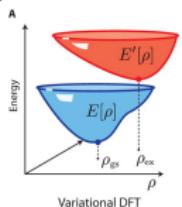
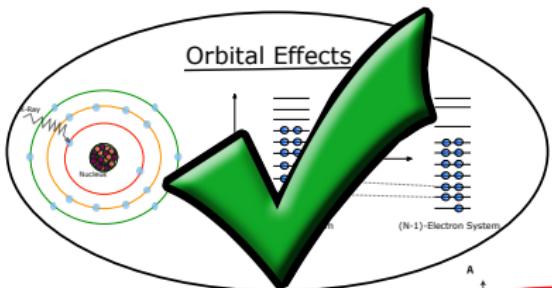
- Compute 10 excitations per hole for each C, N, O 1s orbital in thymine
- Spectra plotted using Gaussians with FWHM of 0.1 eV - 0.4 eV in order to simulate natural spectroscopic broadening effects.

# Full NEXAFS Spectral Simulation: Thymine

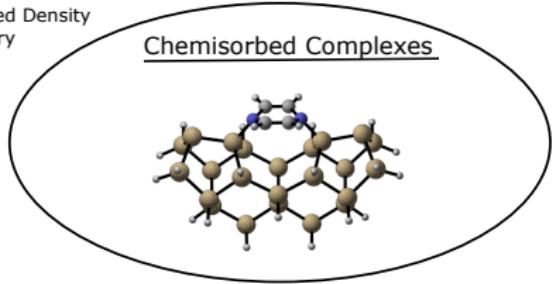
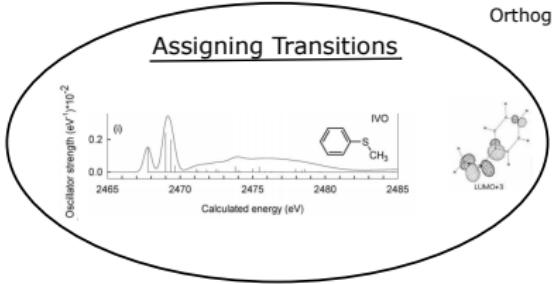


- *Unshifted* OCDFT excitation energies provide excellent comparison to experiment
- Average error of 0.3 eV overall compared to experimental peak maxima

# Treatment of Relativistic Effects In OCDFT



Orthogonality Constrained Density Functional Theory



# Relativistic Effects in Quantum Chemistry Via 2-Component Hamiltonians

- Full Dirac Relativistic equation involves a 4 component Hamiltonian ( $h^D$ ), 2 *large* components (L), 2 *small* components (S)

$$h^D = \begin{pmatrix} h_{LL} & h_{LS} \\ h_{SL} & h_{SS} \end{pmatrix} \quad (9)$$

- Idea is to decouple large and small components of Dirac Hamiltonian through a Foldy-Wouthuysen (FW) unitary transformation to block diagonalize  $h^D$

$$U^\dagger h^D U = U^\dagger \begin{pmatrix} h_{LL} & h_{LS} \\ h_{SL} & h_{SS} \end{pmatrix} U = \begin{pmatrix} h_{++}^{\text{FW}} & 0 \\ 0 & h_{--}^{\text{FW}} \end{pmatrix} \quad (10)$$

- The positive energy contribution is then isolated, which is a sum of relativistic kinetic ( $T^{\text{rel}}$ ) and potential ( $V^{\text{rel}}$ )

$$h_{++}^{\text{FW}} = T^{\text{rel}} + V^{\text{rel}} \quad (11)$$

## Spin-Free Modified Dirac Equation

- Following FW Unitary transformation, the one-electron Dirac equation can be written as:

$$\begin{pmatrix} V & T \\ T & \frac{W}{4c^2} - T \end{pmatrix} \begin{pmatrix} C^L \\ C^S \end{pmatrix} = \begin{pmatrix} S & 0 \\ 0 & \frac{T}{2c^2} \end{pmatrix} \begin{pmatrix} C^L \\ C^S \end{pmatrix} E \quad (12)$$

- Where  $W$  is the relativistic potential which is the sum of spin-free (SF) and spin-orbit (SO) contributions:

$$W = W^{\text{SF}} + W^{\text{SO}} \quad (13)$$

- Neglecting the SO term yields the **spin-free** version of the modified Dirac equation, in AO basis ( $\chi_\mu$ )  $W^{\text{SF}}$  is

$$W_{\mu\nu}^{\text{SF}} = \langle \chi_\mu | \hat{p} \cdot (\hat{V} \hat{p}) | \chi_\nu \rangle \quad (14)$$

## eXact-Two-Component Hamiltonian (X2C)

- Given the form of the unitary transformation of the Dirac Hamiltonian

$$U^\dagger h^D U = \begin{pmatrix} h_{++}^{\text{FW}} & 0 \\ 0 & h_{--}^{\text{FW}} \end{pmatrix}, U = \begin{pmatrix} 1 & -X^\dagger \\ X & 1 \end{pmatrix} \begin{pmatrix} R & 0 \\ 0 & R \end{pmatrix} \quad (15)$$

- X and R are the *coupling* and *renormalization* matrices respectively and relate the MO coefficients of the 2c wavefunction

$$C^S = XC^L \quad C^L = RC^{2c} \quad (16)$$

- In X2C, these relations are used to build the relativistic kinetic and potential energy operators

$$T^{X2C} = R^\dagger(TX + X^\dagger T - X^\dagger TX)R \quad (17)$$

$$V^{X2C} = R^\dagger(V + \frac{1}{4c^2}X^\dagger W^{\text{SF}} X)R \quad (18)$$

## X2C-OCDFT

- Consider the OCDFT energy functional

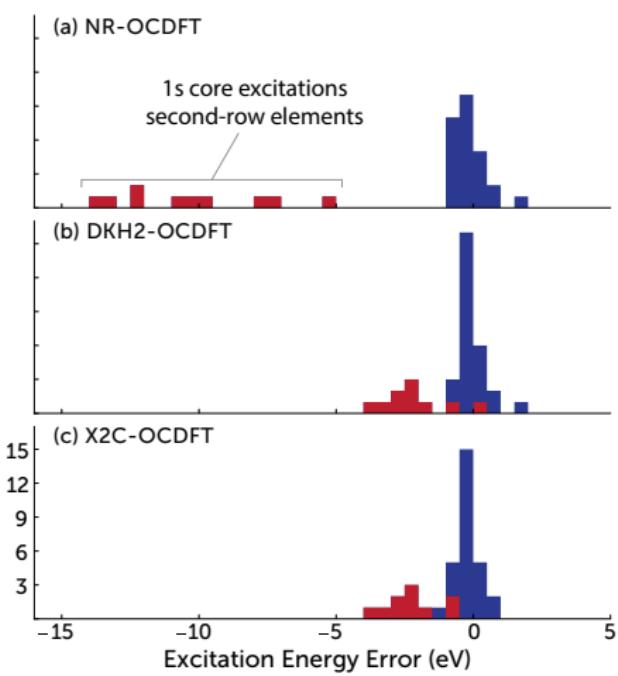
$$E_{\text{OCDFT}}^{(n)}[\{\phi_i^{(n)}\}] = -\frac{1}{2} \sum_i^{\text{occ}} \langle \phi_i^{(n)} | \nabla^2 | \phi_i^{(n)} \rangle + \int d\mathbf{r} v(\mathbf{r}) \rho^{(n)}(\mathbf{r}) + J[\rho^{(n)}] + E_{\text{xc}}^{(0)}[\rho^{(n)}]. \quad (19)$$

- This can be recast in the following matrix form and the *relativistic* X2C kinetic and potential included explicitly

$$E_{\text{OCDFT}}^{(n)}[\{\phi_i^{(n)}\}] = \sum_{\mu\nu} D_{\mu\nu}^{(n)} (T_{\mu\nu}^{\text{X2C}} + V_{\mu\nu}^{\text{X2C}}) + J[\rho^{(n)}] + E_{\text{xc}}^{(0)}[\rho^{(n)}]. \quad (20)$$

- X2C one-electron operator is formed before the SCF cycle and added to the *nonrelativistic* two-electron operators

# X2C-OCDFT Benchmark



- Benchmarked using 37 core-excitations from 13 different molecules
- Calculations done using B3LYP functional and fully uncontracted aug-cc-pVDZ basis set
- MAE for X2C-OCDFT:
  - ▶ 1<sup>st</sup> row: 0.3 eV
  - ▶ 2<sup>nd</sup> row: 0.7 eV

# Relativistic Effects vs. Correlation Effects

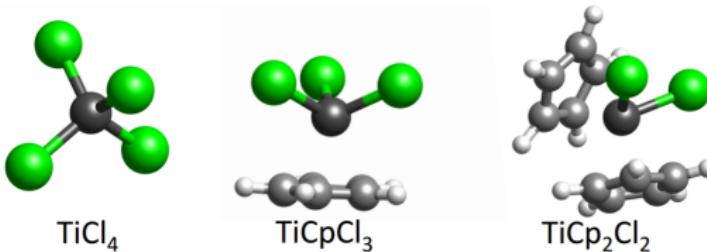
Transitions	Relativistic (eV)	Correlation (eV)
First row 1s	0.2	0.6
Second row 1s	8.0	3.4
Second row 2p	0.5	1.1
All	2.2	1.3

$$\text{Rel} = \text{OCDFT}^{\text{NR}}(E_{\text{xc}}^{\text{B3LYP}}) - \text{OCDFT}^{\text{X2C}}(E_{\text{xc}}^{\text{B3LYP}}) \quad (21)$$

$$\text{Corr} = \text{OCDFT}^{\text{X2C}}(E_{\text{xc}}^{\text{B3LYP}}) - \text{OCDFT}^{\text{X2C}}(E_{\text{x}}^{\text{HF}}) \quad (22)$$

- Proper treatment of electron correlation is more important for 1<sup>st</sup> row elements
- Quickly outpaced by relativistic effects for 2<sup>nd</sup> row
- Proper treatment of relativistic effects will be extremely important for transition metals

# K-Edge of Tetracoordinated Ti Complexes

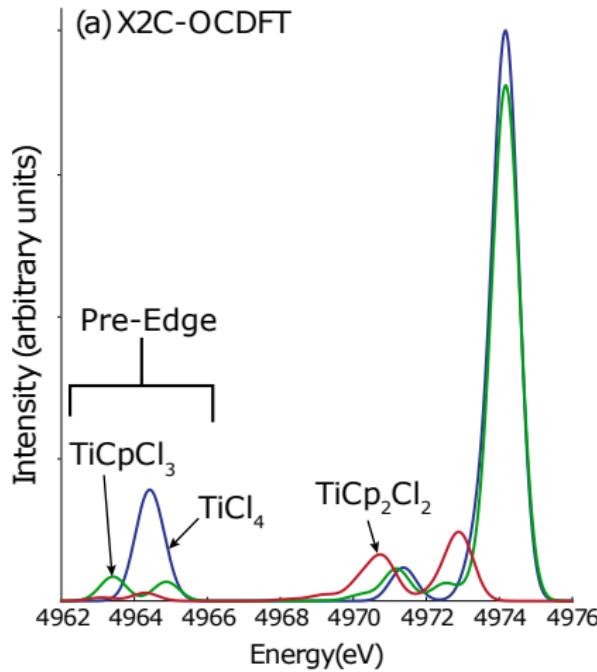


Pre-Edge Contributions for  $\text{TiCl}_4$

State	TDDFT		OCDFT		Exp.
	NR	DKH2	NR	X2C	
1	-107.9	-78.6	-35.6	-5.0	
2	-107.9	-78.6	-35.5	-4.5	
3	-107.0	-77.6	-36.4	-5.7	
4	-106.9	-77.6	-35.3	-4.8	
5	-107.0	-77.7	-36.3	-5.7	

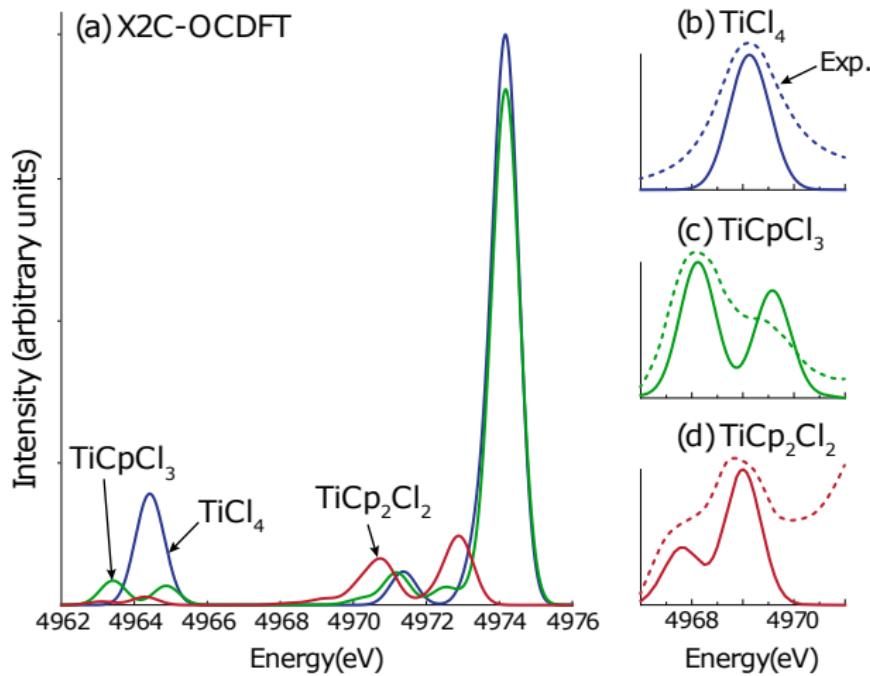
- Pre-edge feature is calculated within  $\approx 5.0$  eV of experiment

# Pre-edge Features of Tetracoordinated Ti Complexes



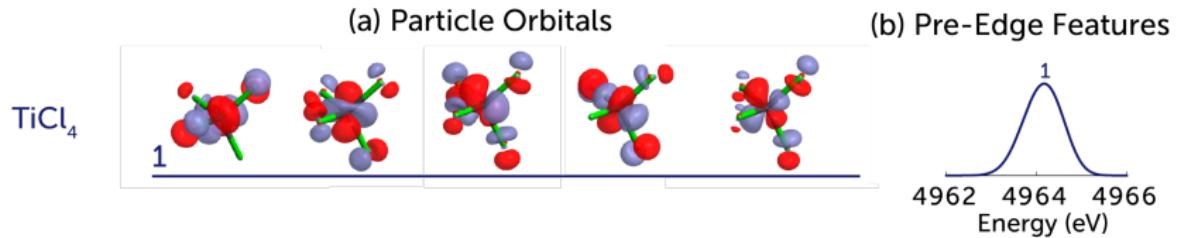
- Pre-edge intensity drop after adding Cp rings to coordination

# Pre-edge Features of Tetracoordinated Ti Complexes



- Peak splitting of pre-edge after adding Cp rings to coordination

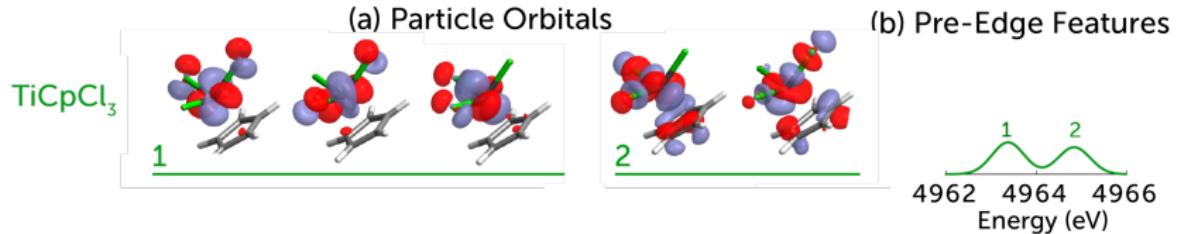
# Particle Orbital Analysis of Pre-Edge $\text{TiCl}_4$



State	$\text{TiCl}_4$	$f$
	Energy	
1	4964.2	0.0945
2	4964.7	0.0940
3	4963.5	0.0002
4	4964.4	0.0947
5	4963.5	0.0000

- All particle orbitals have similar character (i.e. Ti d and Cl p)

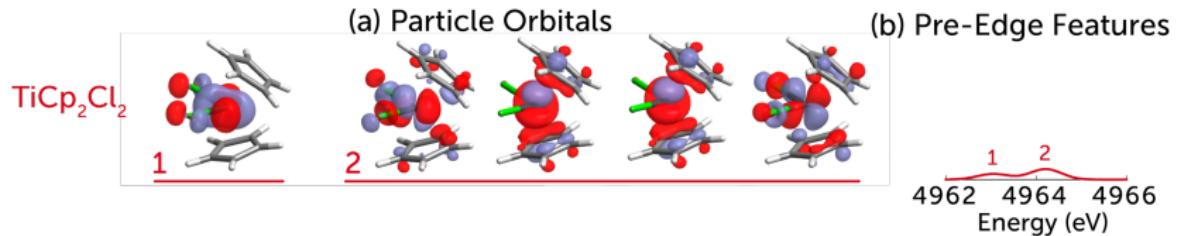
# Particle Orbital Analysis of Pre-Edge $\text{TiCpCl}_3$



State	$\text{TiCpCl}_3$	
	Energy	$f$
1	4963.4	0.0202
2	4963.4	0.0191
3	4963.5	0.0164
4	4964.9	0.0220
5	4963.9	0.0217

- States with significant Cp ring contributions are pushed to higher energy

# Particle Orbital Analysis of Pre-Edge $\text{TiCp}_2\text{Cl}_2$



State	$\text{TiCp}_2\text{Cl}_2$	
	Energy	$f$
1	4963.1	0.0078
2	4964.3	0.0121
3	4964.4	0.0009
4	4964.4	0.0000
5	4964.3	0.0055

- States with significant Cp ring contributions are pushed to higher energy

# Further Investigation of Pre-Edge Intensity

- Pre-edge intensity will be evaluated using the following methods:
  - ▶ Natural population analysis using JANPA software
  - ▶ Atomic decomposition of the total dipole moment
- We can decompose the total dipole moment in the following fashion

$$\mu_{0n} = \langle \Phi^{(n)} | \hat{\mathbf{r}} | \Phi^{(0)} \rangle = \sum_{\mu\nu} D_{\mu\nu}^{0n} \langle \chi_\mu | \hat{\mathbf{r}} | \chi_\nu \rangle \quad (23)$$

- From here we can do a restricted sum over donor/acceptor atom and angular momentum shell

$$\mu_{0n}(A_{l_A} \rightarrow B_{l_B}) = \sum_{\mu \in A_{l_A}} \sum_{\nu \in B_{l_B}} D_{\mu\nu}^{0n} \langle \chi_\mu | \mathbf{r} | \chi_\nu \rangle \quad (24)$$

# Further Investigation of Pre-Edge Intensity

## Natural Population Analysis

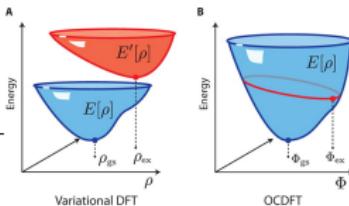
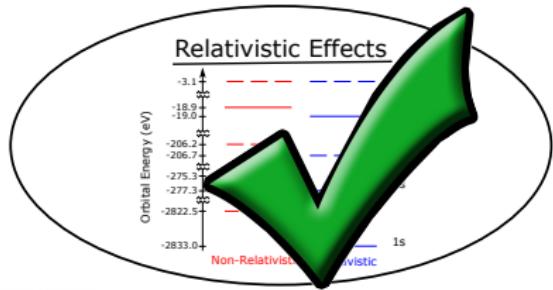
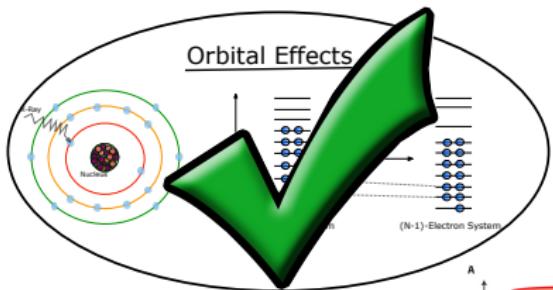
State	$\Delta Ti_p$			$\Delta Cl_p$			$\Delta Ti_d$		
	TiCl <sub>4</sub>	TiCpCl <sub>3</sub>	TiCp <sub>2</sub> Cl <sub>2</sub>	TiCl <sub>4</sub>	TiCpCl <sub>3</sub>	TiCp <sub>2</sub> Cl <sub>2</sub>	TiCl <sub>4</sub>	TiCpCl <sub>3</sub>	TiCp <sub>2</sub> Cl <sub>2</sub>
1	0.0107	0.0066	0.0097	-0.2184	-0.0597	0.0051	1.1348	1.1614	1.2586

## Atomic Decomposition of Dipole Moments

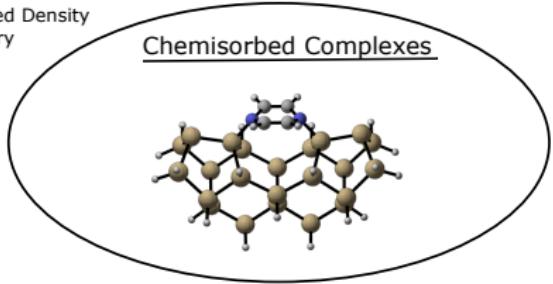
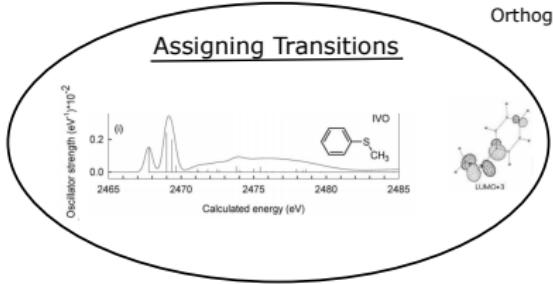
Contribution	$\mu_x$	$\mu_y$	$\mu_z$	$ \mu $
<b>State 1</b>				
Ti <sub>s</sub> → Ti <sub>p</sub>	-0.000395	-0.000079	-0.000113	0.000418
Cl <sub>p</sub> → Cl <sub>p</sub>	+0.000062	+0.000012	+0.000018	0.000066
Ti <sub>s</sub> → Cl <sub>p</sub>	-0.000006	+0.000003	-0.000064	0.000064
Other	-0.000007	+0.000002	+0.000073	0.000073

- Population analysis shows that the transitions are 1s → 3d
- Largest dipole contribution is Ti<sub>s</sub> → Ti<sub>d</sub>

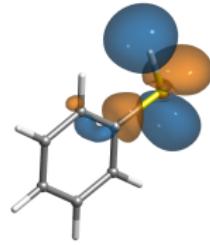
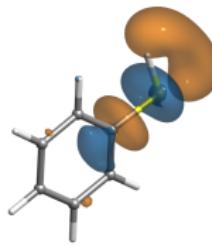
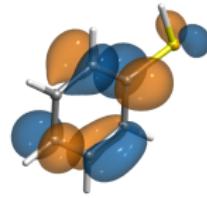
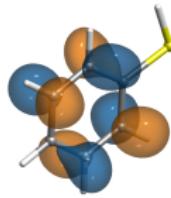
# Overview of Dissertation Work



Orthogonality Constrained Density Functional Theory



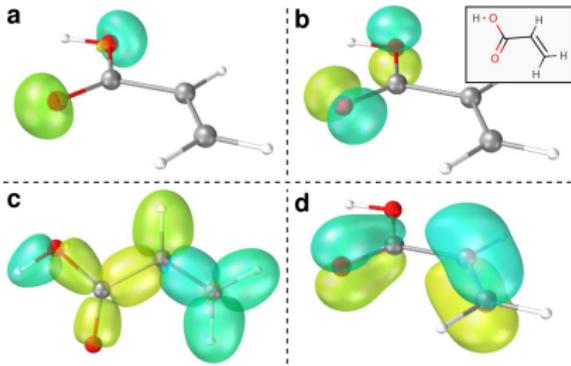
# Assigning the Character of Particle Orbitals

 $\phi_p^1$  $\phi_p^2$  $\phi_p^3$  $\phi_p^4$ 

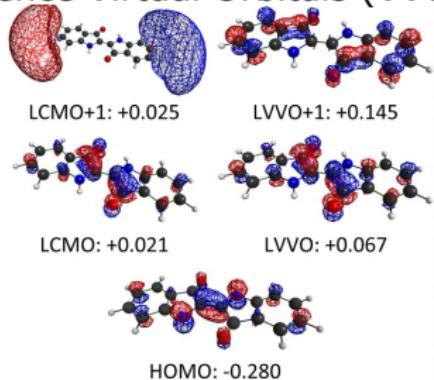
- $\phi_p^1$  and  $\phi_p^2$  clearly have contributions from both  $\sigma_{S-C}^*$  and  $\sigma_{S-H}^*$  how do you make a definitive assignment?
- How to differentiate between the two unique  $\pi_{C=C}^*$  orbitals?
- Desirable to find method to quantify localized orbital contributions

# Localized and Minimal Orbital Sets in Quantum Chemistry

## Intrinsic Bond Orbitals (IBOs)



## Valence Virtual Orbitals (VVOs)



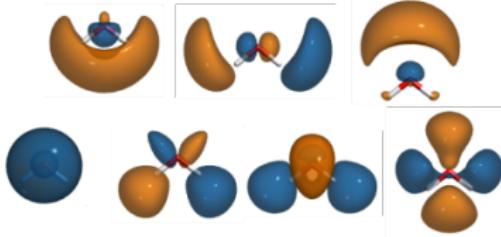
- Sets like the IBOs<sup>1</sup> and VVOs<sup>2</sup> aim to analyze electronic wavefunctions using orbitals that are:
  - ▶ More compact
  - ▶ Easier to interpret
  - ▶ More chemically relevant
- Can we build a similar set to analyze bonding contributions to particle orbitals in OCDFT?

<sup>1</sup>G. Knizia. *J. Chem. Theory Comput.* **2013**

<sup>2</sup>M. W. Schmidt; E. A. Hull; T. L. Windus. *J. Phys. Chem. A.* **2015**

# Localized Intrinsic Valence Virtual Orbitals

(A) Canonical molecular orbitals (CMOs)

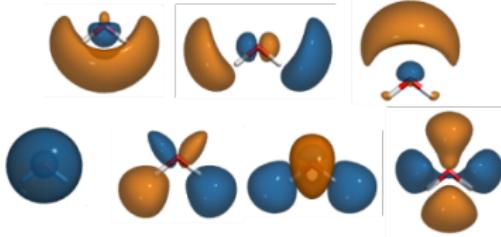


- Start with a set of virtual canonical molecular orbitals (CMOs) expanded in an atom-centered basis  $\{\chi_\mu\}$

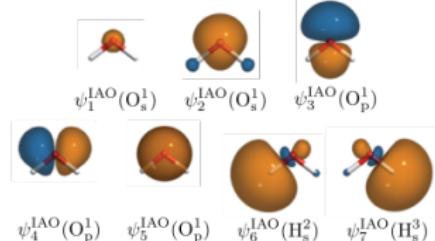
$$|\phi_a\rangle = \sum_{\mu}^{N_{AO}} |\chi_{\mu}\rangle C_{\mu a}, \quad a = 1, \dots, N_{vir} \quad (25)$$

# Localized Intrinsic Valence Virtual Orbitals

(A) Canonical molecular orbitals (CMOs)



(B) Intrinsic atomic orbitals (IAOs)



- Evaluate overlap ( $\mathbf{S}$ ) with set of Intrinsic Atomic Orbitals (IAOs)

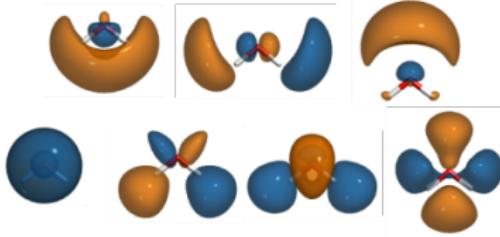
$$(\mathbf{S})_{a\rho} = \langle \phi_a | \psi_\rho^{\text{IAO}} \rangle \quad (26)$$

- Where IAOs are defined as

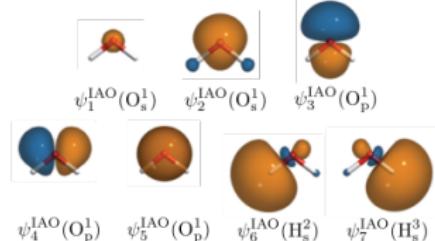
$$|\psi_\rho^{\text{IAO}}\rangle = \sum_\mu^{N_{\text{AO}}} |\chi_\mu\rangle \tilde{C}_{\mu\rho}, \quad \rho = 1, \dots, N_{\text{IAO}}$$

# Localized Intrinsic Valence Virtual Orbitals

(A) Canonical molecular orbitals (CMOs)



(B) Intrinsic atomic orbitals (IAOs)



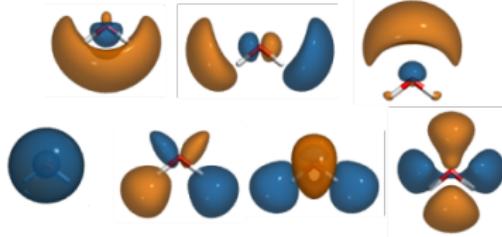
- Perform SVD of overlap matrix to get orthogonal transformation matrices  $\mathbf{U}$  and  $\mathbf{V}$

$$\mathbf{S} = \mathbf{U}\sigma\mathbf{V}^\dagger \quad (27)$$

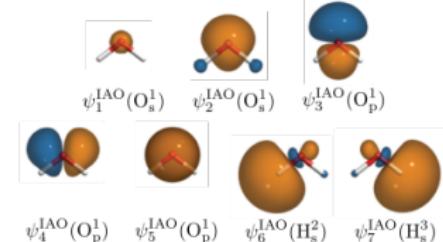
- $\mathbf{U}$  and  $\mathbf{V}$  are rotations of the virtual and IAO space respectively that achieve maximum coincidence

# Localized Intrinsic Valence Virtual Orbitals

(A) Canonical molecular orbitals (CMOs)



(B) Intrinsic atomic orbitals (IAOs)



LIMO Procedure

A) and (B)

SVD of overlap matrix

(C) Valence virtual orbitals (VVOs)

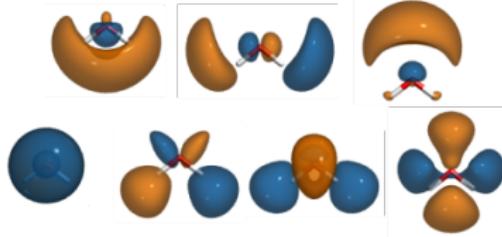


- Use  $\mathbf{U}$  to transform canonical virtuals into valence virtual orbitals (VVOs):

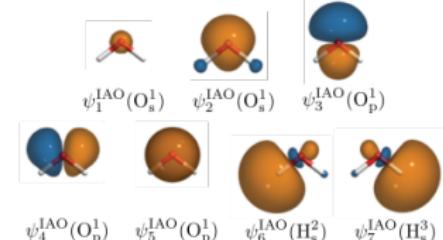
$$|\psi_v^{\text{VVO}}\rangle = \sum_a^{N_{\text{vir}}} |\phi_a\rangle U_{av}, \quad v = 1, \dots, N_{\text{VVO}}. \quad (28)$$

# Localized Intrinsic Valence Virtual Orbitals

(A) Canonical molecular orbitals (CMOs)



(B) Intrinsic atomic orbitals (IAOs)



LIVVO Procedure

(A) and (B)

SVD of overlap matrix

(C) Valence virtual orbitals (VVOs)



Pipek-Mezey Localization

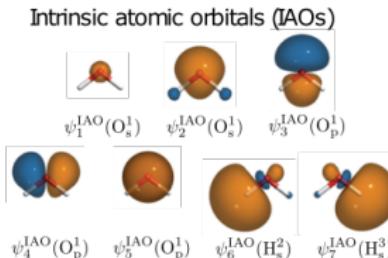
(D) Localized intrinsic VVOs (LIVVOs)



- Pipek-Mezey localization can be employed in order to yield an orbital set that represents each valence antibonding interaction in the molecular environment
- This yields LIVVOs, need to assign their atomic character

# Determining Atomic Character of IAOs

- Atomic character is assigned using a Mulliken Population Analysis



Gross Populations

$A_l$	$\psi_1^{\text{IAO}}$	$\psi_2^{\text{IAO}}$	$\psi_3^{\text{IAO}}$	$\psi_4^{\text{IAO}}$	$\psi_5^{\text{IAO}}$	$\psi_6^{\text{IAO}}$	$\psi_7^{\text{IAO}}$
$\text{O}_s^1$	1.00	1.16	0.00	0.00	0.00	-0.08	-0.08
$\text{O}_p^1$	0.00	0.00	1.04	1.11	1.00	-0.07	-0.07
$\text{H}_s^2$	0.00	-0.08	-0.02	-0.05	0.00	1.18	-0.03
$\text{H}_s^3$	0.00	-0.08	-0.02	-0.05	0.00	-0.03	1.18

- We compute the population matrix ( $P_{\mu\nu}$ ) for each IAO as:

$$P_{\mu\nu}(\rho) = \tilde{C}_{\mu\rho} S_{\mu\nu} \tilde{C}_{\nu\rho}, \quad \rho = 1, \dots, N_{\text{IAO}} \quad (29)$$

- Gross populations on each atom  $A$  and angular momentum shell  $l$  are obtained via partial sums of  $P_{\mu\nu}$

$$\text{GP}_{A_l}(\rho) = \sum_{\mu \in A_l} \sum_{\nu}^{N_{\text{AO}}} P_{\mu\nu}(\rho) \quad (30)$$

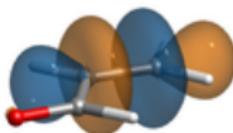
- character of each IAO chosen as maximum  $\text{GP}_{A_l}(\rho)$  contribution

# Using IAOs to Classify LIVVOs

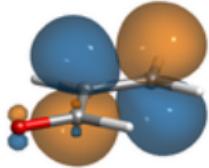
- Overlap of each LIVVO ( $\psi_l^{\text{LIVVO}}$ ) with the IAOs ( $\psi_\rho^{\text{IAO}}$ ) is evaluated:

$$S'_{l\rho} = |\langle \psi_l^{\text{LIVVO}} | \psi_\rho^{\text{IAO}} \rangle|^2 \quad (31)$$

- Assign antibonding interaction ( $\sigma^*, \pi^*, \dots$ ) of LIVVOs based on atomic character (s,p,...) of IAOs



$$\begin{aligned} &= 0.20 \psi^{\text{IAO}}(\text{C}_s^2) + 0.24 \psi^{\text{IAO}}(\text{C}_p^2) \\ &\quad + 0.20 \psi^{\text{IAO}}(\text{C}_s^3) + 0.25 \psi^{\text{IAO}}(\text{C}_p^3) = \sigma_{\text{C}^2-\text{C}^3}^* \end{aligned}$$

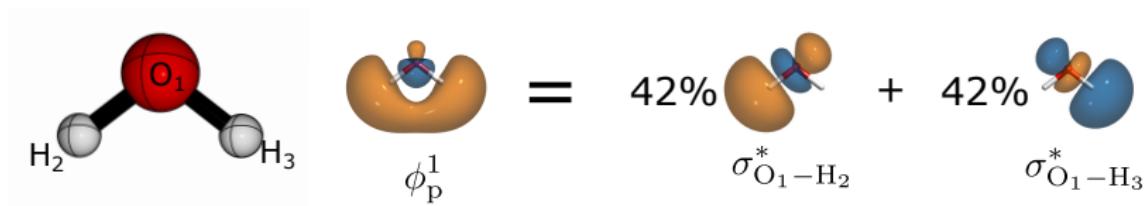


$$= 0.47 \psi^{\text{IAO}}(\text{C}_p^2) + 0.51 \psi^{\text{IAO}}(\text{C}_p^3) = \pi_{\text{C}^2-\text{C}^3}^*$$

# Assigning Orbital Character of OCDFT Particle Orbitals

- Character of the particle orbital  $\phi_p^{(n)}$  by evaluating its overlap with each LIVVO ( $\psi_l^{\text{LIVVO}}$ )

$$\Omega_{pl}^{(n)} = |\langle \phi_p^{(n)} | \psi_l^{\text{LIVVO}} \rangle|^2. \quad (32)$$

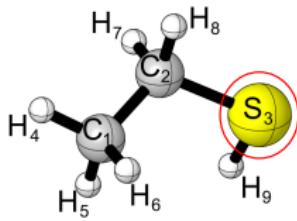


- Total valence character can be quantified by summing all LIVVO contributions. (84% for above  $\text{H}_2\text{O}$  example)

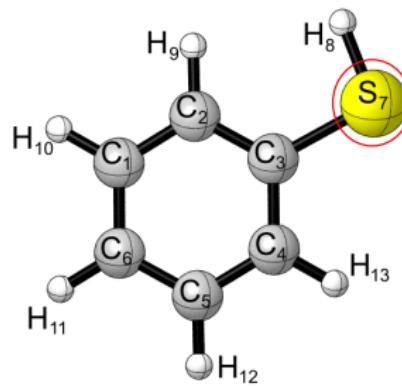
$$t_{\text{p}}^{\text{val},(n)} = \sum_l^{N_{\text{LIVVO}}} \Omega_{pl}^{(n)}. \quad (33)$$

# Assigning Transitions in S K-edge of Ethanethiol and Benzenethiol

- Spectra are calculated with OCDFT at the B3LYP/jun-cc-pVTZ level of theory

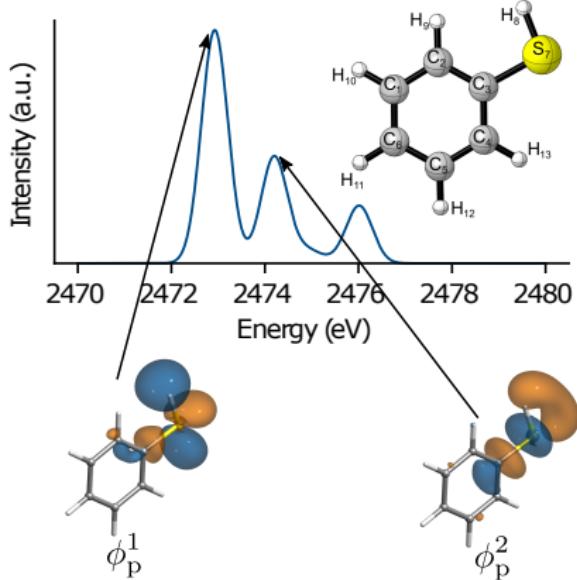
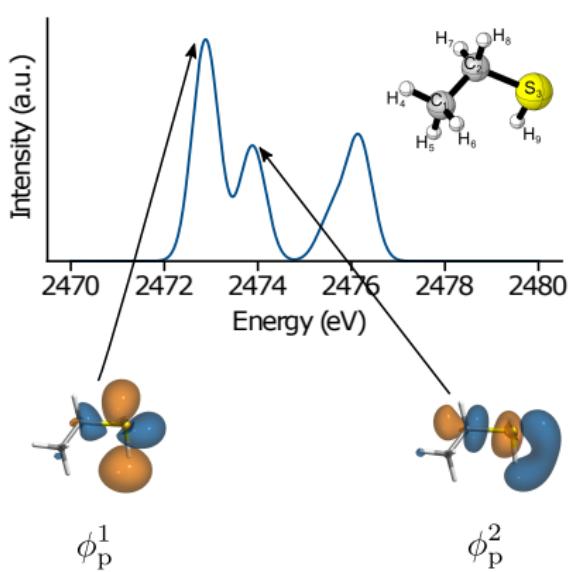


Ethanethiol



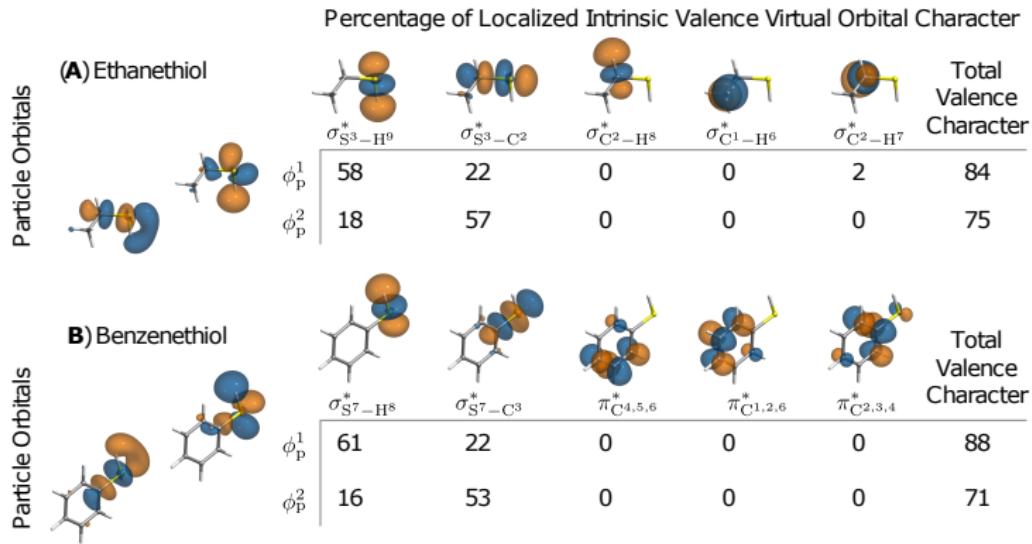
Benzenethiol

# What are the local contributions to $\phi_p^1$ and $\phi_p^2$ ?



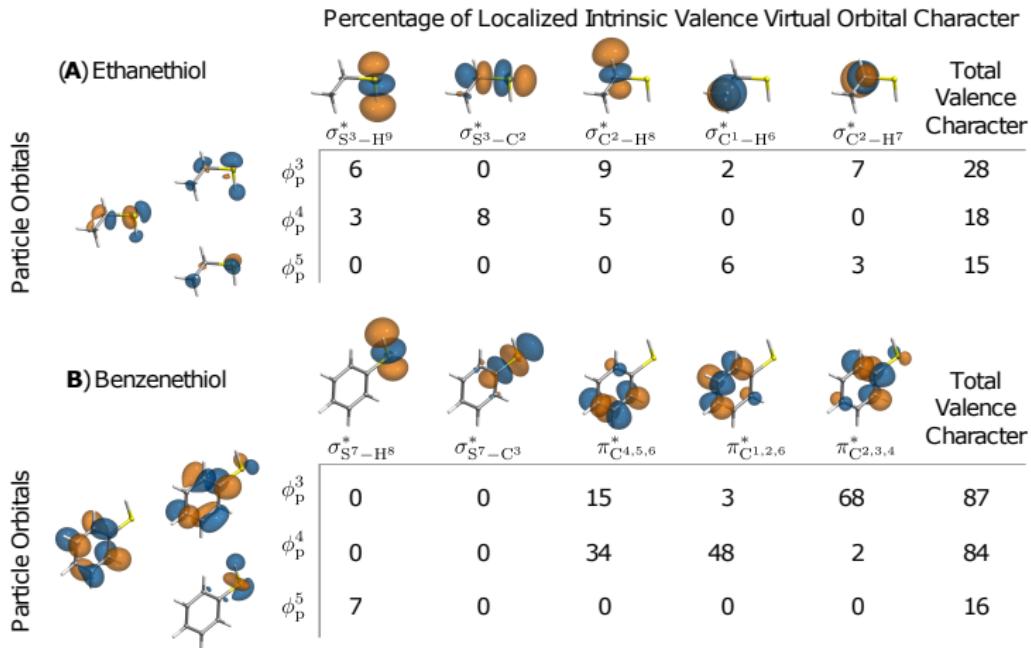
- Particle orbitals contain orbital character along S – C and S – H
- What is the contribution of the thiol bond to each excited state?

# What are the local contributions to $\phi_p^1$ and $\phi_p^2$ ?



- LIVVO analysis yields *unambiguous* assignment for each particle orbital
- Thiol bond is large contributor to first peak, weak contributor to second peak

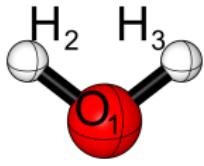
# Other Contributions to the S K-Edge



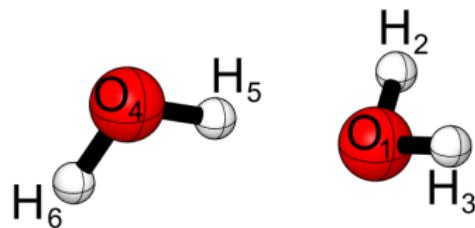
- $\phi_p^3$  and  $\phi_p^4$  localized away from S atom in benzenethiol, results in lower intensity

# Effect of Hydrogen Bonding on O K-Edge of Water

- Spectra are calculated with OCDFT at the B3LYP/jun-cc-pVTZ level of theory

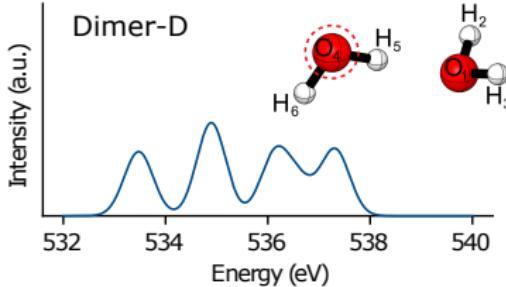
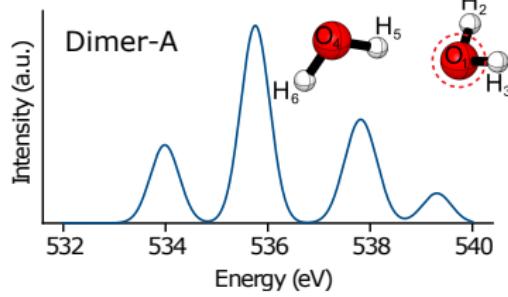
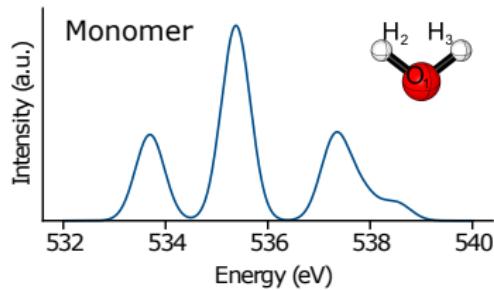


Monomer



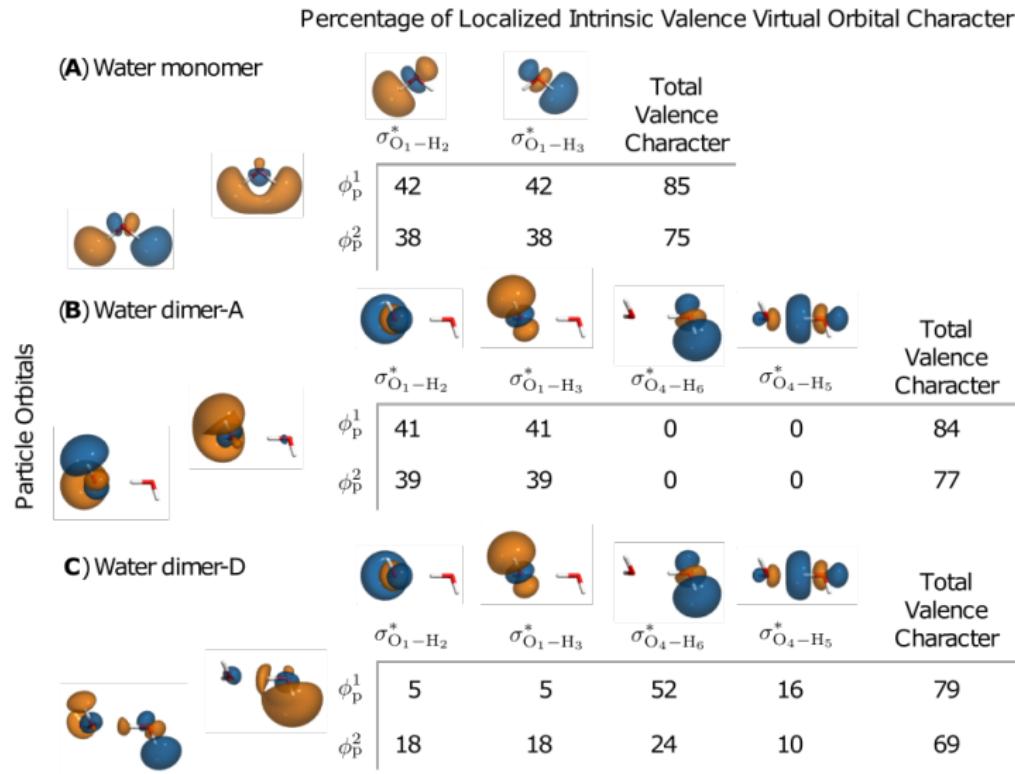
Dimer

# Effect of Hydrogen Bonding on O K-Edge of Water

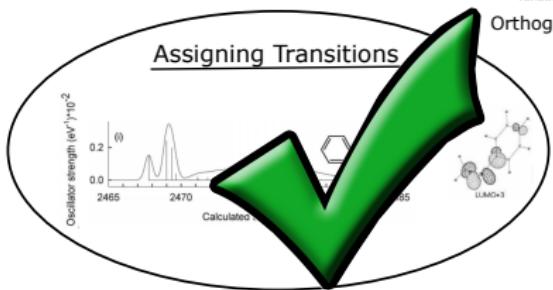
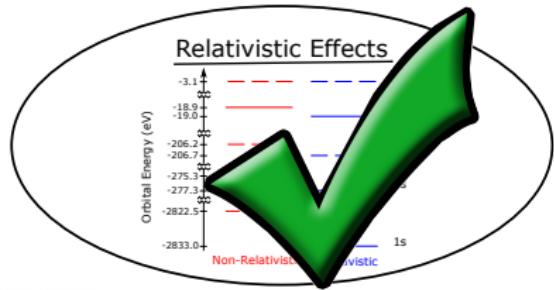
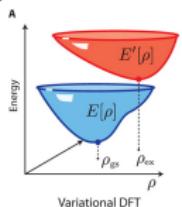
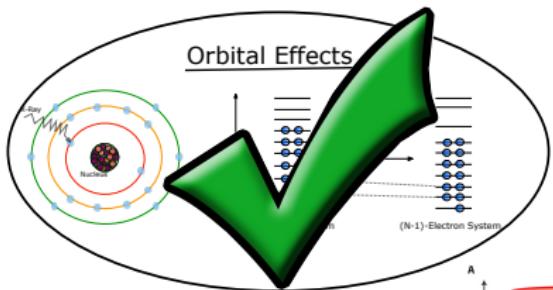


- Accepting H-bond (Dimer-A) has small effect on spectral features, donating H-bond (Dimer-D) has significant effect

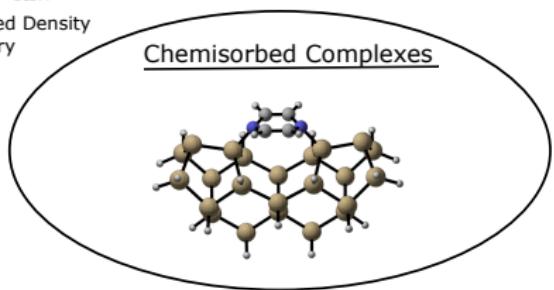
# Effect of Hydrogen Bonding on O K-Edge of Water



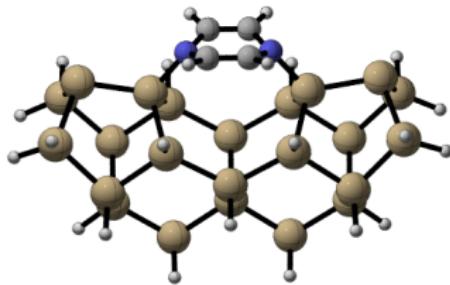
# Overview of Dissertation Work



Orthogonality Constrained Density Functional Theory



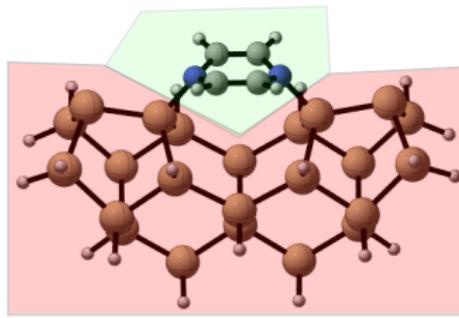
# Organic Core-Excitations in Chemisorbed Molecules



Pyrazine ( $C_4H_4N_2$ ) on Si(100)

- Appropriate surface cluster models contain at least 10 or more surface atoms

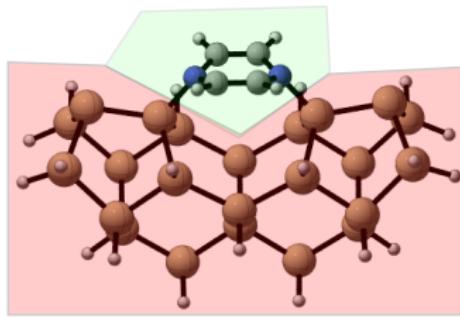
# Organic Core-Excitations in Chemisorbed Molecules



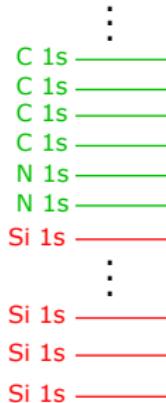
Pyrazine ( $C_4H_4N_2$ ) on Si(100)

- Appropriate surface cluster models contain at least 10 or more surface atoms
- Model complexes contain the organic **adsorbate** attached to a **surface cluster**

# Organic Core-Excitations in Chemisorbed Molecules



Pyrazine ( $C_4H_4N_2$ ) on Si(100)



Orbital Diagram

- Lowest energy core orbitals are associated with the **surface cluster**
- Presents an algorithmic challenge for original OCDFT algorithm
- Need a method to specifically target core orbitals of the **organic adsorbate**

## Maximum Subspace Occupation (MSO) Approach

- Consider a set of atomic orbital basis functions ( $\varphi_s$ ) ordered by atom center, principal quantum number, and angular momentum
- We can build an operator that spans a subset ( $s$ ) of AOs

$$\hat{\Gamma}_s = \sum_s |\varphi_s\rangle\langle\varphi_s| \quad (34)$$

- Evaluate an atomic orbital occupation number ( $\Omega_i$ ) for each occupied molecular orbital ( $\phi_i$ ) within the desired subspace

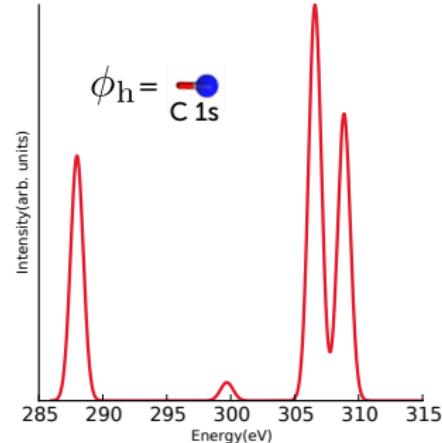
$$\Omega_i = \langle \phi_i | \hat{\Gamma}_s | \phi_i \rangle = \sum_s \langle \phi_i | \varphi_s \rangle \langle \varphi_s | \phi_i \rangle. \quad (35)$$

- Hole orbital ( $\phi_h$ ) is now chosen from a subset of the occupied orbitals where  $\Omega_i$  is greater than a user-defined occupation threshold parameter

# MSO-OCDFT: CO Example

	$\phi_i$	$\Omega_i$
5A <sub>1</sub>		0.008
1B <sub>2</sub>		0.000
1B <sub>1</sub>		0.000
4A <sub>1</sub>		0.008
3A <sub>1</sub>		0.007
2A <sub>1</sub>		0.976
1A <sub>1</sub>		0.000

a) Evaluate Subspace occupation of each occupied orbital for C 1s subspace



b) Hole orbital is chosen as the C 1s orbital. C K-Edge is calculated directly.

- C 1s orbital is targeted based on its occupation in the C 1s atomic orbital subset
- Note: Due to locality of core orbitals, threshold can be set fairly high

# MSO-OCDFT: Consistency of Energy and $f_{osc}$

- Test calculations done on  $CCl_4$  using both the standard algorithm and MSO-OCDFT

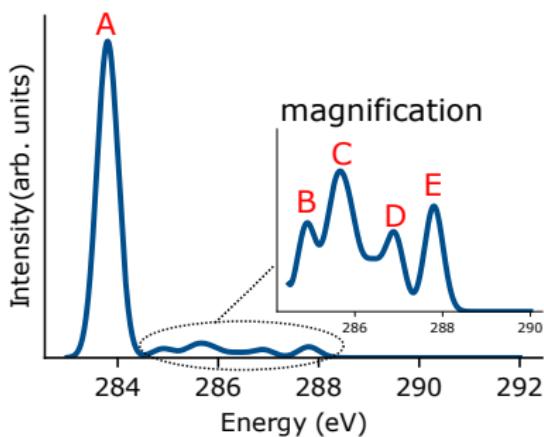
First 3 C core excitations in  $CCl_4$

State	OCDFT		MSO-OCDFT	
	$\omega$ (eV)	$f_{osc}$	$\omega$ (eV)	$f_{osc}$
1	292.0002	0.0000	292.0005	0.0000
2	292.7093	0.0384	292.7097	0.0384
3	292.6669	0.0385	292.6659	0.0385

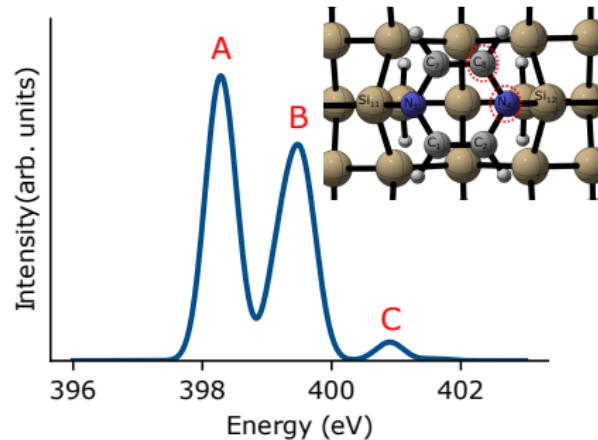
- Negligible differences between the two results
- Validates that this is a good approximation to full orthogonal set of solutions

# C and N K-Edge of Pyrazine

a) C 1s Excitation Spectrum



b) N 1s Excitation Spectrum



- Able to target C and N core efficiently with MSO-OCDFT
- 10 excited states were targeted for each spectrum
- Without MSO:
  - ▶ 230 Si Excitations would have been necessary to calculate before N K-edge
  - ▶ 230 Si + 20 N excitations would have been necessary before the C K-edge

## Concluding Remarks

- OCDFT has been extended and proven successful for calculating core-excited
- Full Treatment of relativistic effects were included via the X2C Hamiltonian and
- A Localized set of orbitals has been introduced and used to quantify local contributions to the OCDFT particle orbitals
- An approach to target specific hole orbitals based on occupation in an AO subset has been introduced and allows for the calculation core-excited states of chemisorbed organic complexes.

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Evangelista Lab Members



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York



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Sam



CiCi

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Charles  
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(Dad)



Glenda  
Derricotte  
(Mom)



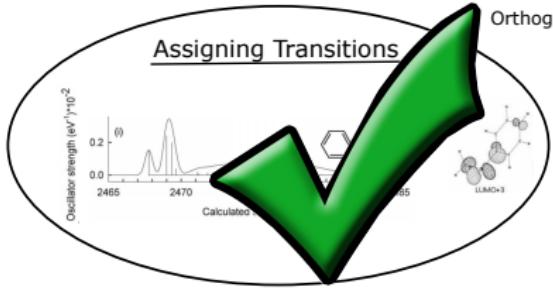
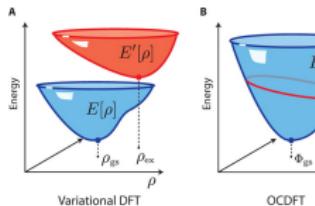
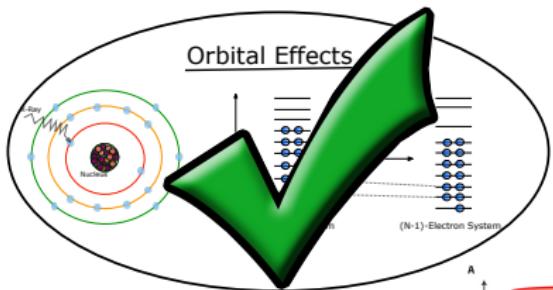
Alencia  
Derricotte  
(Wife)



Charles  
Derricotte  
(Brother)

"Family and friendships are two of the greatest facilitators of happiness."  
– John C. Maxwell

# Thank You!



Orthogonality Constrained Density Functional Theory

