

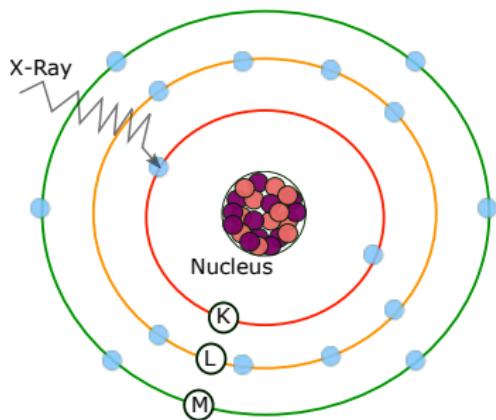
Development and Applications of Orthogonality Constrained Density Functional Theory for the Accurate Simulation X-Ray Absorption Spectroscopy

Wallace Derricotte

Dissertation Defense

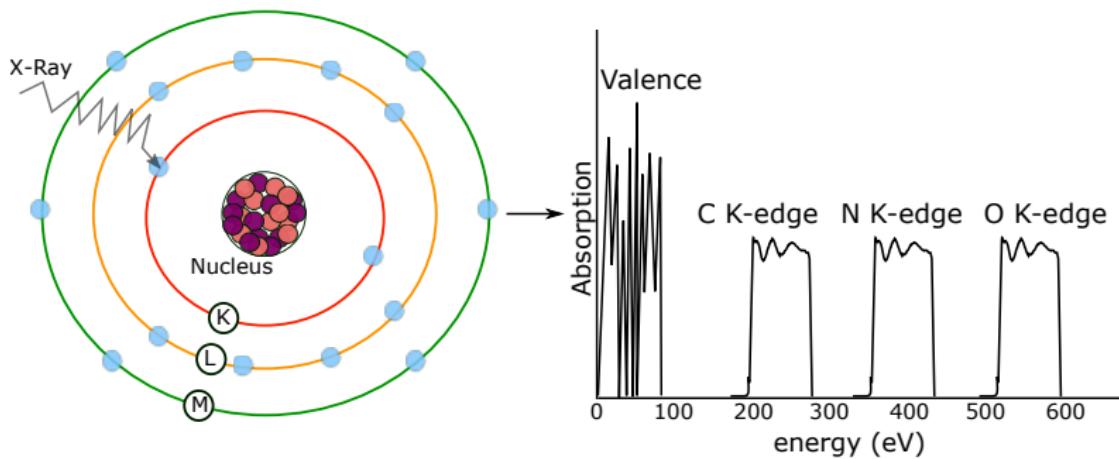
June 28th, 2017

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

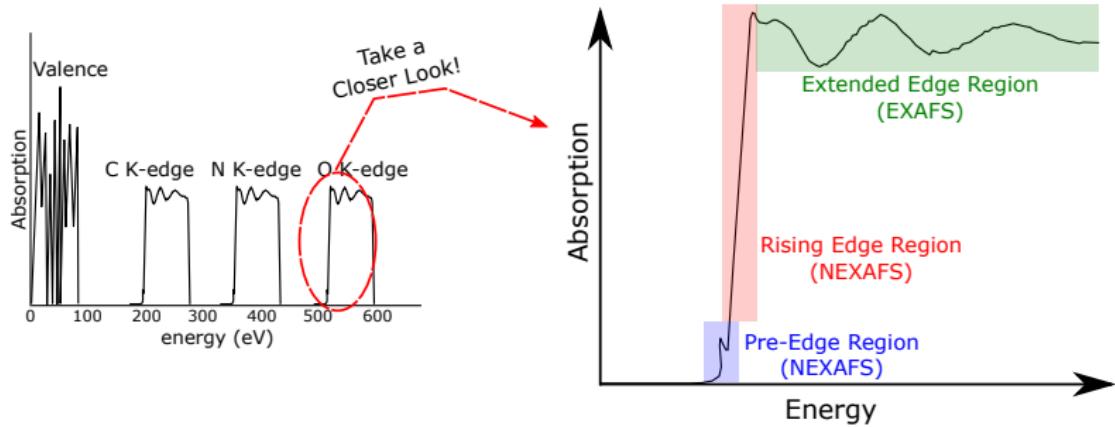
X-ray Absorption Mechanism: Core-Excited States



- 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 number¹(K=1, L=2, M=3)

¹J. 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 region¹

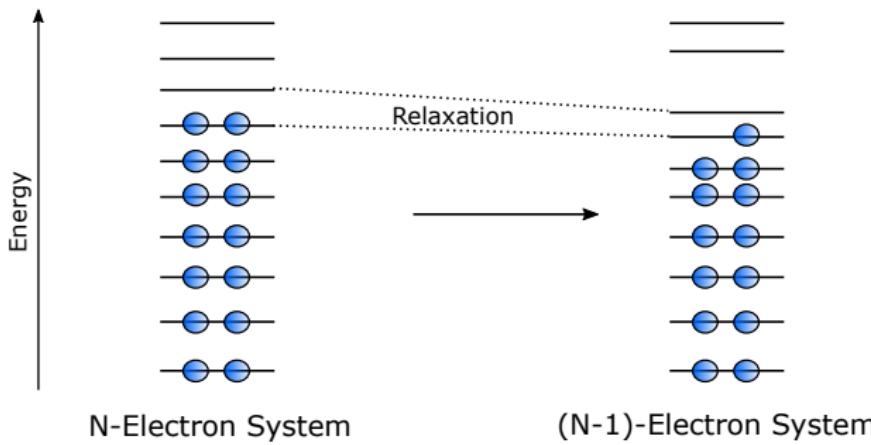
¹B. K. Teo. EXAFS: Basic Principles and Data Analysis; Springer: 2012

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)
 - ▶ RASSCF
 - ▶ 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 Δ SCF
- All theoretical methods face unique theoretical challenges when calculating core excited states

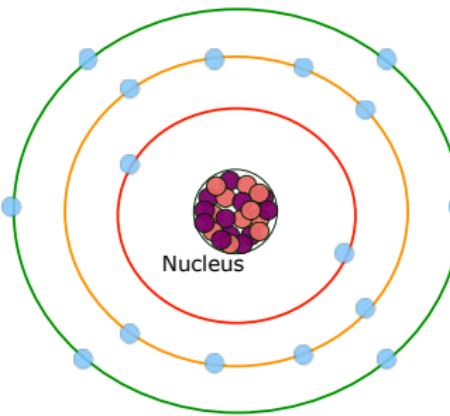
Theoretical Challenges: Orbital Relaxation

- 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

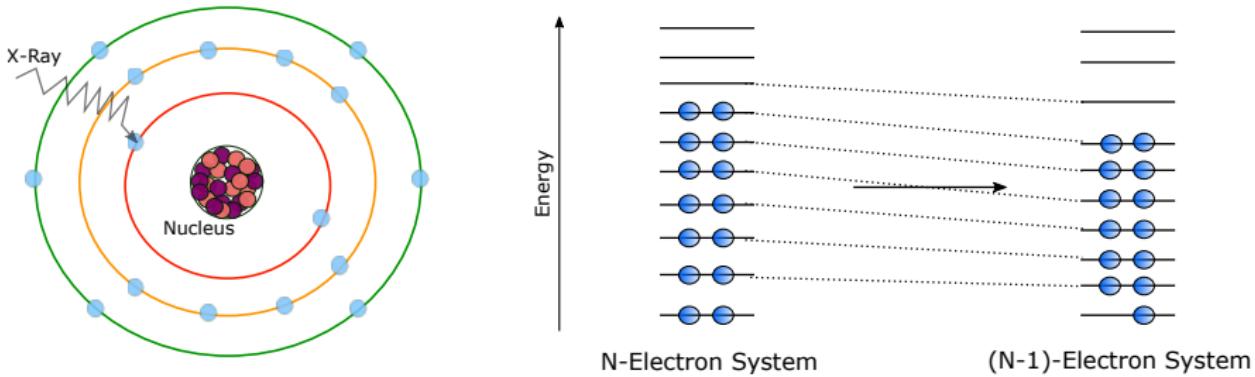


- Effective nuclear charge (Z_{eff}) on any electron can be approximated as:

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

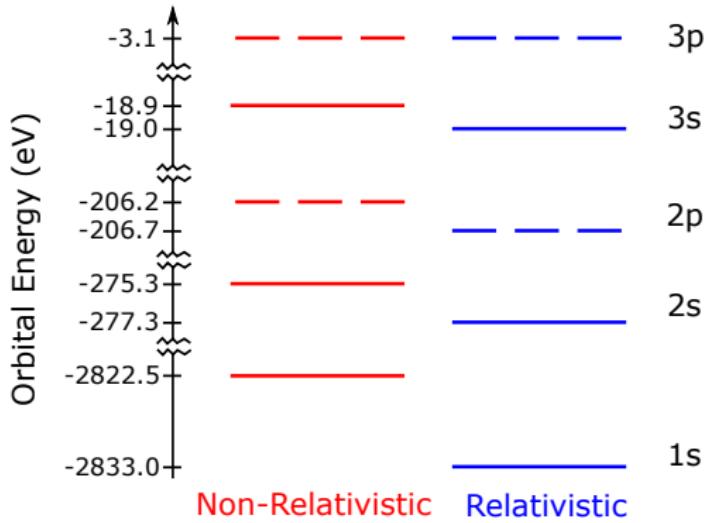
- where Z is the number of protons and σ is the average number of electrons b/w the nucleus and the electron in question

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

Theoretical Challenges: Relativistic Effects



Orbital energies of 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 (H_2O) and silane (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 2nd order Douglas-Kroll-Hess Hamiltonian.¹ All calculations were performed using the ORCA software package.

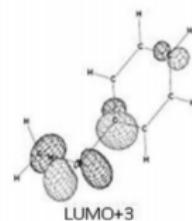
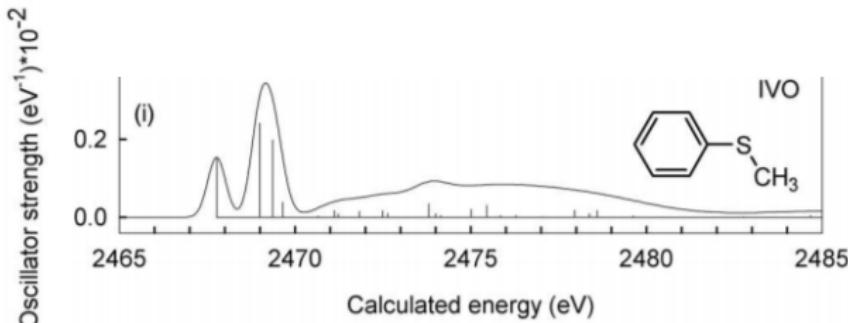
H_2O		SiH_4		
	O 1s	LUMO	Si 1s	LUMO
NR-UHF	−555.88	7.17	−1858.20	5.02
R-UHF	−556.34	7.16	−1863.04	5.03

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

¹M. Reiher. *Theor. Chem. Acc.*. 2006

Theoretical Challenges: Assigning Excited States

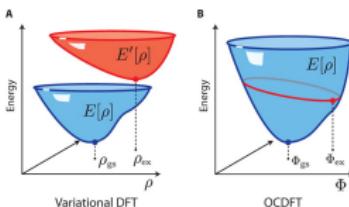
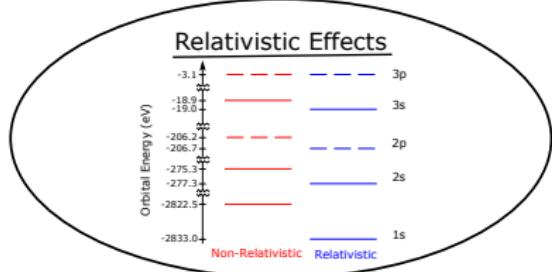
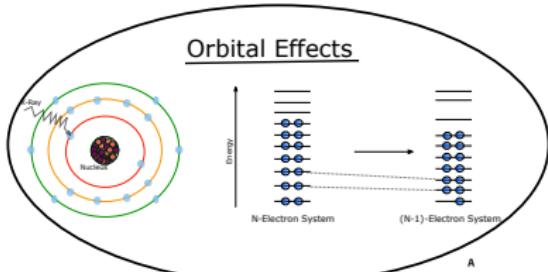
- Excited states are often assigned based on MO plots relative to the ground state



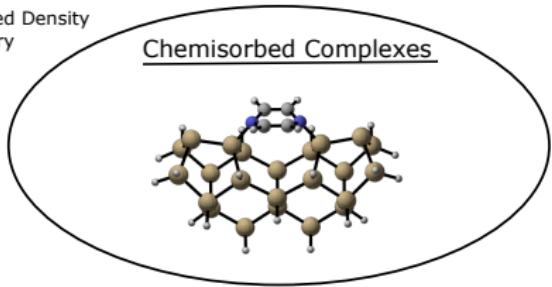
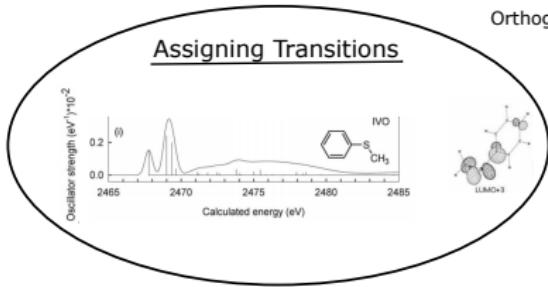
- LUMO+3 for methylsulfanyl benzene above was assigned as $\pi^*(\text{C}=\text{C})$,¹ but other contributions are clearly present
- Two issues with this type of assignment
 - Assignments based on MO plots are potentially ambiguous
 - Approach is not systematic/reproducible

¹S. Behyan; Y. Hu; S. G. Urquhart. *J. Chem. Phys.* 2013

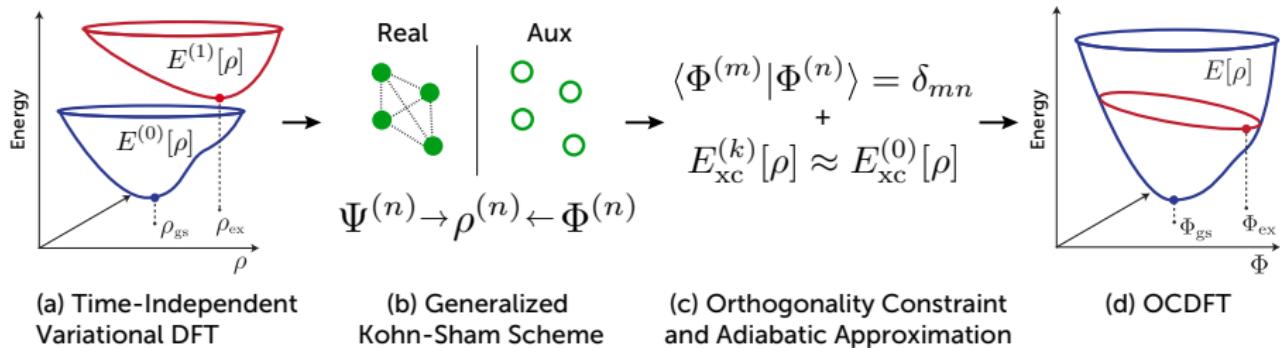
Overview of Dissertation Work



Orthogonality Constrained Density Functional Theory



Orthogonality Constrained Density Functional Theory

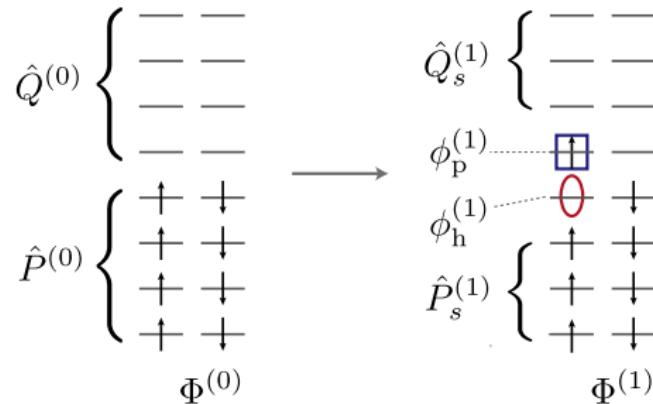


- Variational time-independent (TI) formulation of density functional theory (DFT)¹
- This choice of constraint prevents **variational collapse** of the excited state SCF
- OCDFT excited state functional can be written as:

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

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

OCDFT: Minimal Orthogonality Conditions



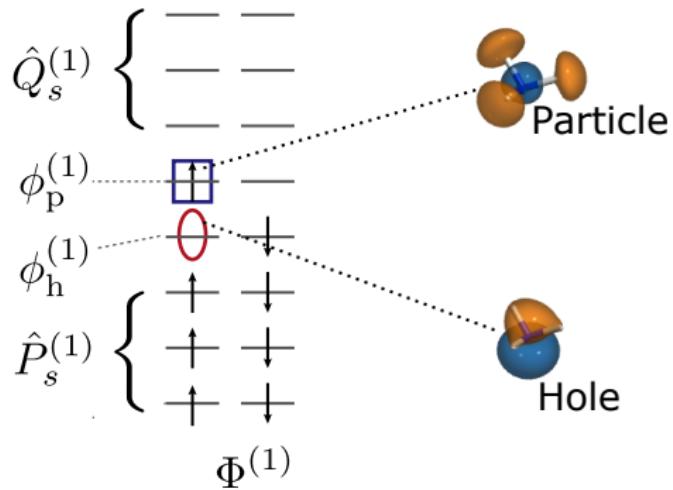
- Enforcing orthogonality introduces a *hole* ($\phi_h^{(1)}$) and *particle* ($\phi_p^{(1)}$) orbital that must satisfy the following:

$$\hat{Q}^{(0)} \phi_h^{(1)} = 0, \quad (2)$$

$$\hat{P}^{(0)} \phi_p^{(1)} = 0, \quad (3)$$

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

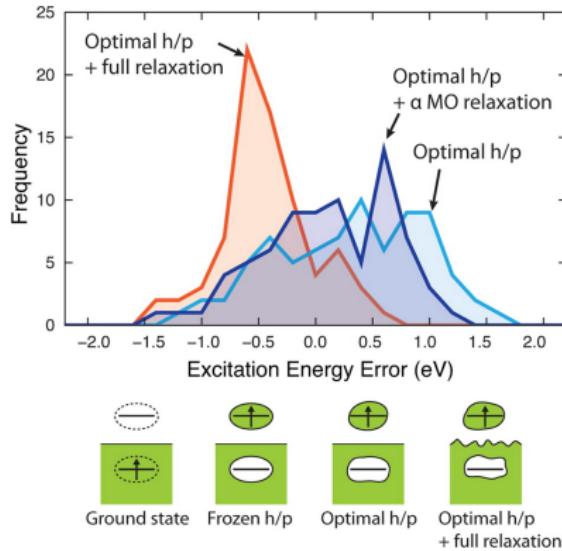
OCDFT: Hole and Particle Orbitals in Practice



Particle orbitals for first excited state in 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

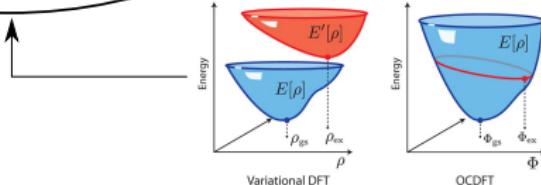
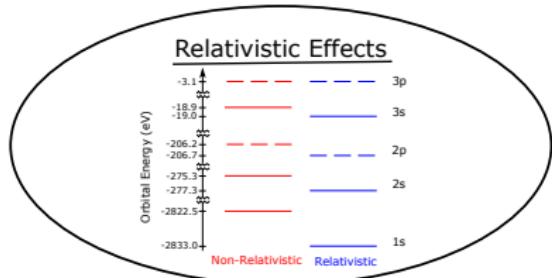
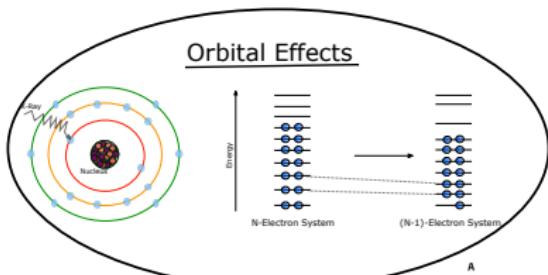
Treatment of Orbital Relaxation in OCDFT



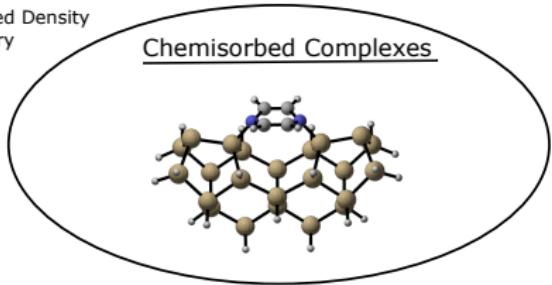
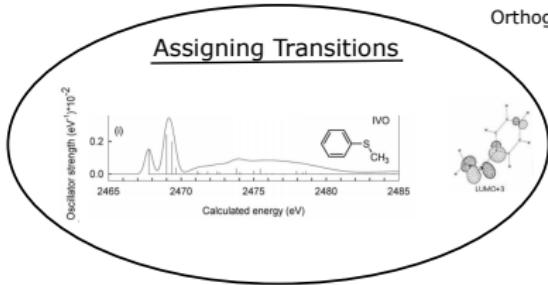
- Original tests on valence excitation showed full inclusion of relaxation effects yielded best results¹
- If the theory is extended to core excitation we can benefit from full inclusion of orbital relaxation

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

Developing OCDFT For Core-Excited States

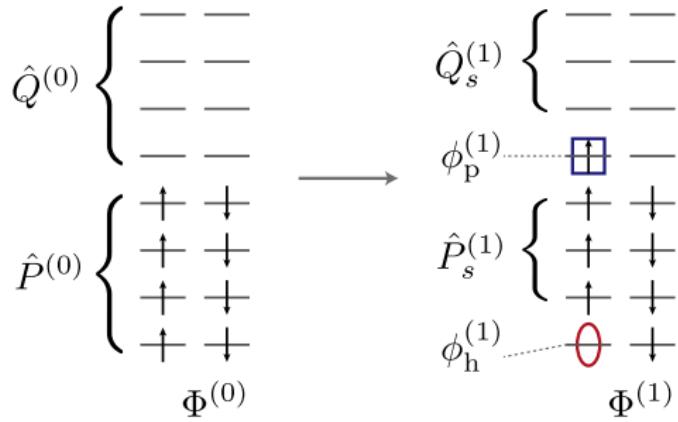


Orthogonality Constrained Density Functional Theory



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



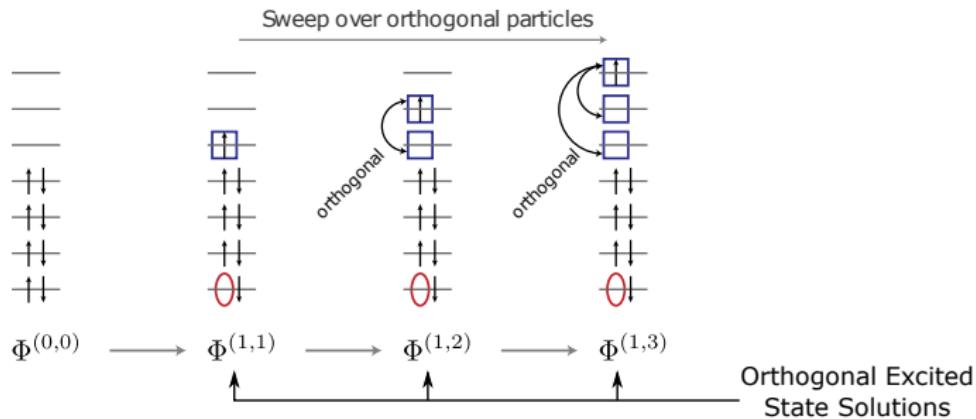
Extension of OCDFT For NEXAFS Spectral Simulation

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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

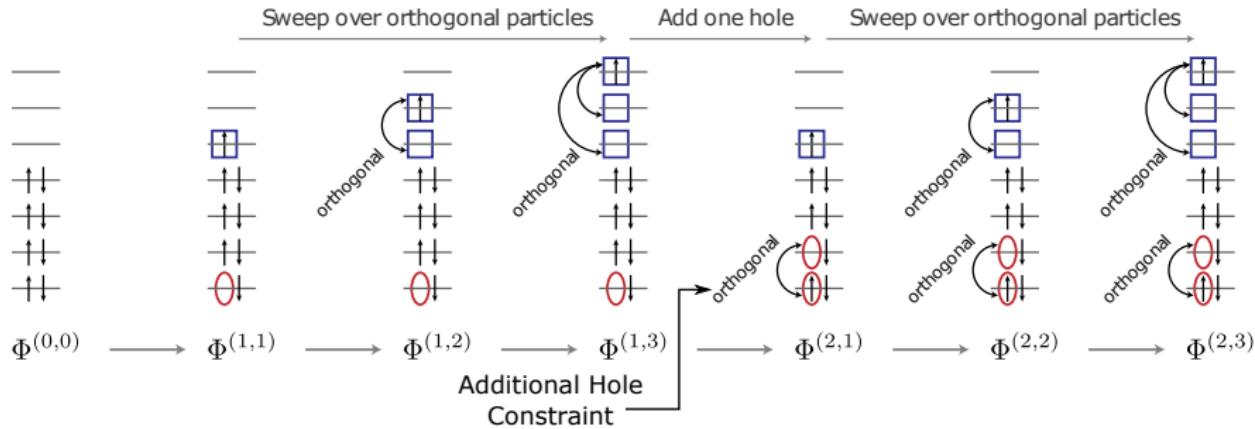
Extension of OCDFT For NEXAFS Spectral Simulation



- 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 orthogonal set:

$$\langle \phi_p^{(1,a)} | \phi_p^{(1,b)} \rangle = \delta_{ab}, \quad \forall a, b \leq n_u. \quad (4)$$

Extension of OCDFT For NEXAFS Spectral Simulation

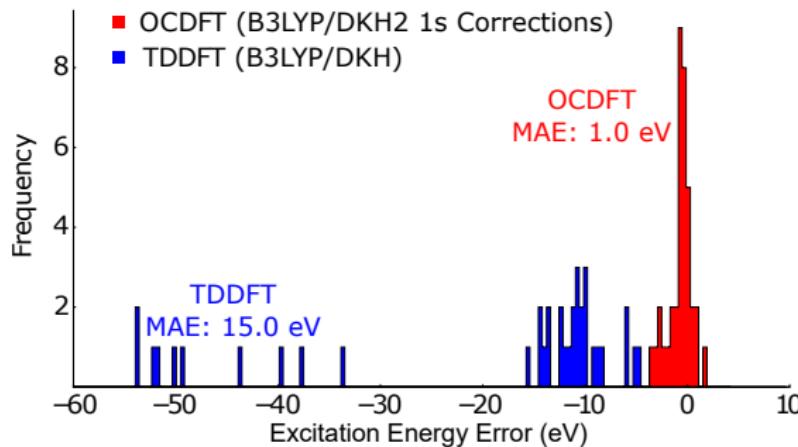


- Increase core index by one and sweep through another series of core-excited solutions: $\Phi^{(2,1)}, \Phi^{(2,2)}, \dots, \Phi^{(2,n_u)}$.
- Where an additional constraint is added to the hole orbital to be orthogonal to the hole orbital of the first sweep:

$$\langle \phi_h^{(1,1)} | \phi_h^{(2,a)} \rangle = 0, \quad \forall a \leq n_u. \quad (5)$$

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:

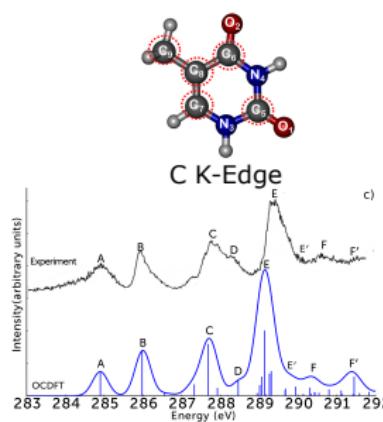
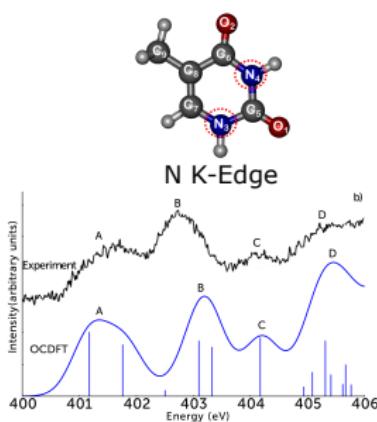
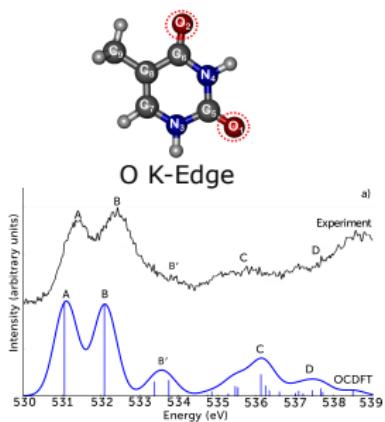
$$\mu_{n0} = \langle \Phi^{(n)} | \hat{\mathbf{r}} | \Phi^{(0)} \rangle \quad (6)$$

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

$$f_{\text{osc}} = \frac{2}{3} |\mu_{n0}|^2 \omega_n \quad (7)$$

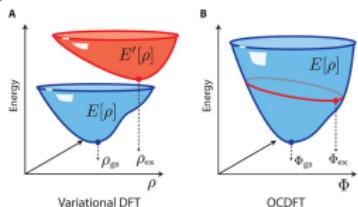
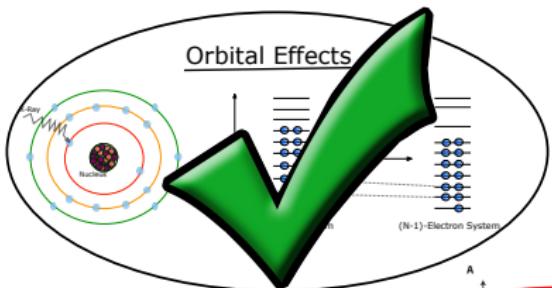
- Compute 10 excitations per hole for each C, N, O 1s orbital in thymine
- Spectra plotted using Gaussians with FWHM of 0.1 eV - 0.4 eV in order to simulate natural spectroscopic broadening effects.

Full NEXAFS Spectral Simulation: Thymine

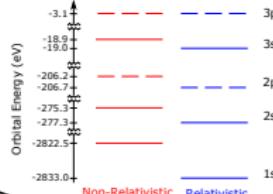


- *Unshifted* OCDFT excitation energies provide excellent comparison to experiment
- Average error of 0.3 eV overall compared to experimental peak maxima

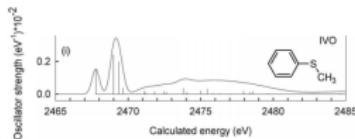
Treatment of Relativistic Effects In OCDFT



Relativistic Effects

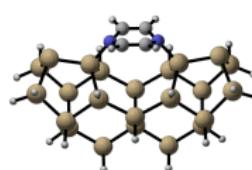


Assigning Transitions



Orthogonality Constrained Density Functional Theory

Chemisorbed Complexes



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)

$$h^D = \begin{pmatrix} h_{LL} & h_{LS} \\ h_{SL} & h_{SS} \end{pmatrix} \quad (8)$$

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

$$U^\dagger h^D U = U^\dagger \begin{pmatrix} h_{LL} & h_{LS} \\ h_{SL} & h_{SS} \end{pmatrix} U = \begin{pmatrix} h_{++}^{\text{FW}} & 0 \\ 0 & h_{--}^{\text{FW}} \end{pmatrix} \quad (9)$$

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

$$h_{++}^{\text{FW}} = T^{\text{rel}} + V^{\text{rel}} \quad (10)$$

Spin-Free Modified Dirac Equation

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

$$\begin{pmatrix} V & T \\ T & \frac{W}{4c^2} - T \end{pmatrix} \begin{pmatrix} C^L \\ C^S \end{pmatrix} = \begin{pmatrix} S & 0 \\ 0 & \frac{T}{2c^2} \end{pmatrix} \begin{pmatrix} C^L \\ C^S \end{pmatrix} E \quad (11)$$

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

$$W = W^{\text{SF}} + W^{\text{SO}} \quad (12)$$

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

$$W_{\mu\nu}^{\text{SF}} = \langle \chi_\mu | \hat{p} \cdot (\hat{V} \hat{p}) | \chi_\nu \rangle \quad (13)$$

eXact-Two-Component Hamiltonian (X2C)

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

$$U^\dagger h^D U = \begin{pmatrix} h_{++}^{\text{FW}} & 0 \\ 0 & h_{--}^{\text{FW}} \end{pmatrix}, U = \begin{pmatrix} 1 & -X^\dagger \\ X & 1 \end{pmatrix} \begin{pmatrix} R & 0 \\ 0 & R \end{pmatrix} \quad (14)$$

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

$$C^S = XC^L \quad C^L = RC^{2c} \quad (15)$$

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

$$T^{X2C} = R^\dagger(TX + X^\dagger T - X^\dagger TX)R \quad (16)$$

$$V^{X2C} = R^\dagger(V + \frac{1}{4c^2}X^\dagger W^{\text{SF}} X)R \quad (17)$$

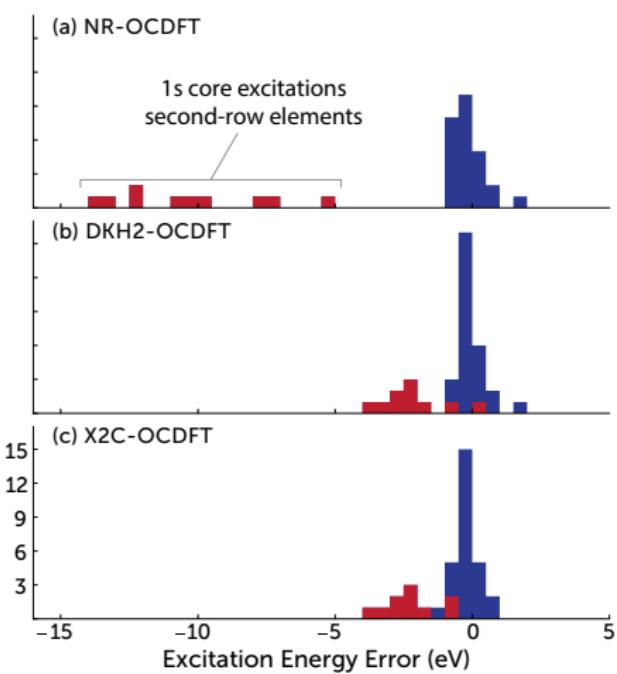
X2C-OCDFT

- The *relativistic* X2C kinetic and potential terms are now included in the OCDFT energy functional

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

- 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:
 - ▶ 1st row: 0.3 eV
 - ▶ 2nd row: 0.7 eV

Relativistic Effects vs. Correlation Effects

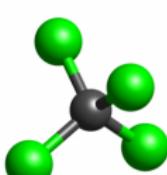
Transitions	Relativistic (eV)	Correlation (eV)
First row 1s	0.2	0.6
Second row 1s	8.0	3.4
Second row 2p	0.5	1.1
All	2.2	1.3

$$\text{Rel} = \text{OCDFT}^{\text{NR}}(E_{\text{xc}}^{\text{B3LYP}}) - \text{OCDFT}^{\text{X2C}}(E_{\text{xc}}^{\text{B3LYP}}) \quad (18)$$

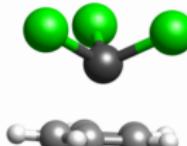
$$\text{Corr} = \text{OCDFT}^{\text{X2C}}(E_{\text{xc}}^{\text{B3LYP}}) - \text{OCDFT}^{\text{X2C}}(E_{\text{x}}^{\text{HF}}) \quad (19)$$

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

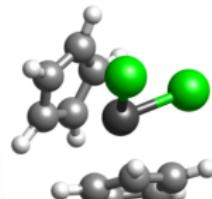
K-Edge of Tetracoordinated Ti Complexes



TiCl₄



TiCpCl₃

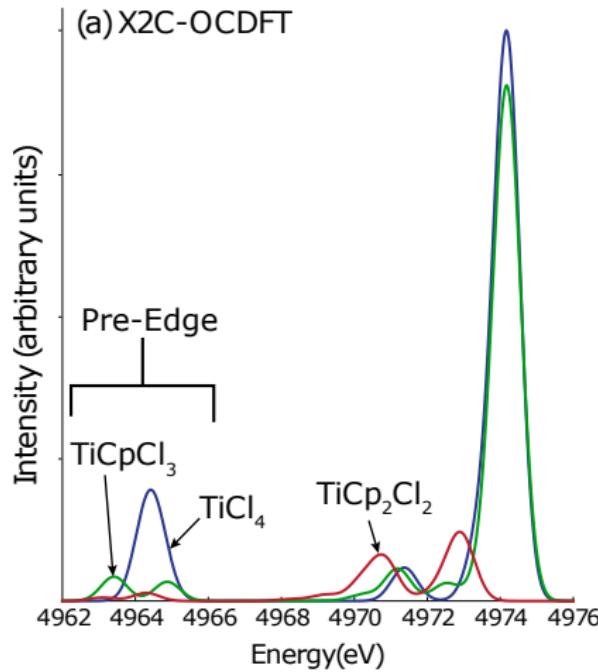


TiCp₂Cl₂

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	

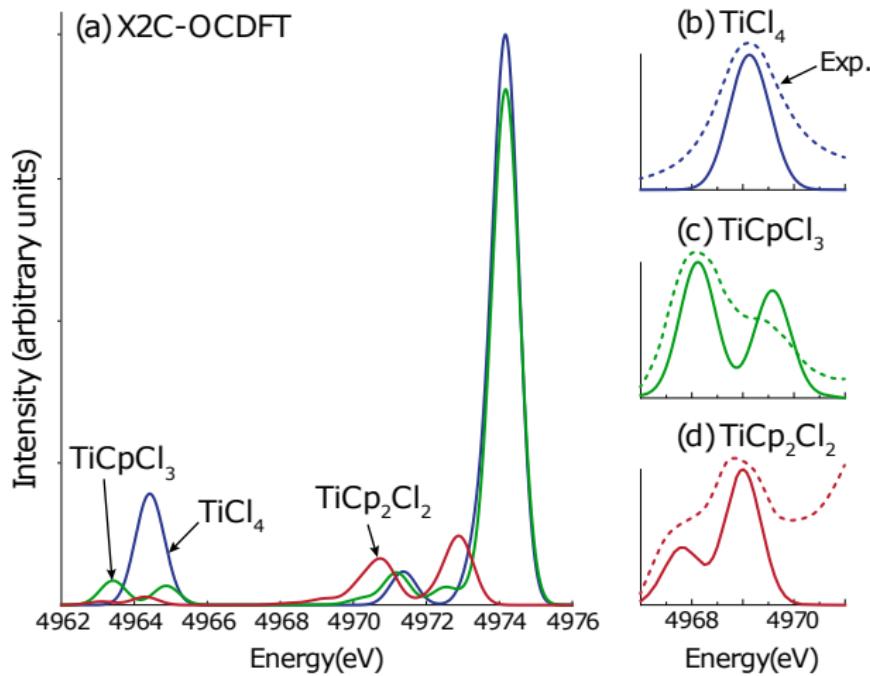
- Pre-edge feature is calculated within ≈ 5.0 eV of experiment

Pre-edge Features of Tetracoordinated Ti Complexes



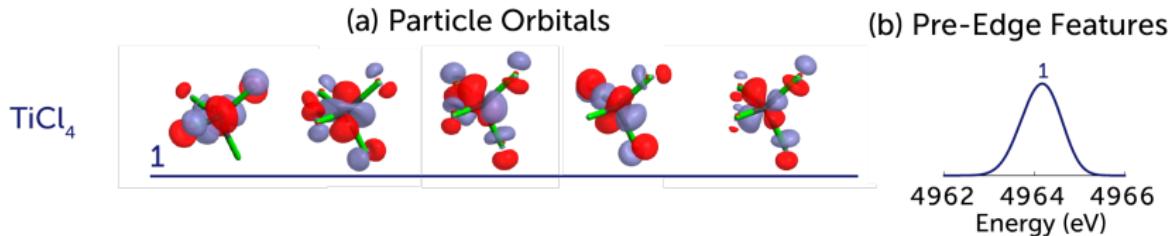
- Pre-edge intensity drop after adding Cp rings to coordination

Pre-edge Features of Tetracoordinated Ti Complexes



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

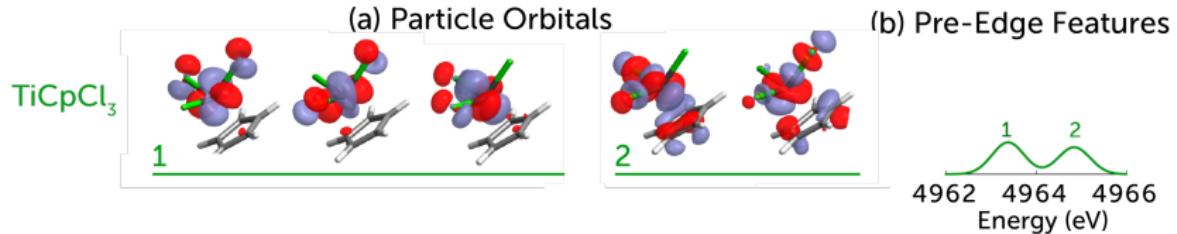
Particle Orbital Analysis of Pre-Edge TiCl_4



State	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)

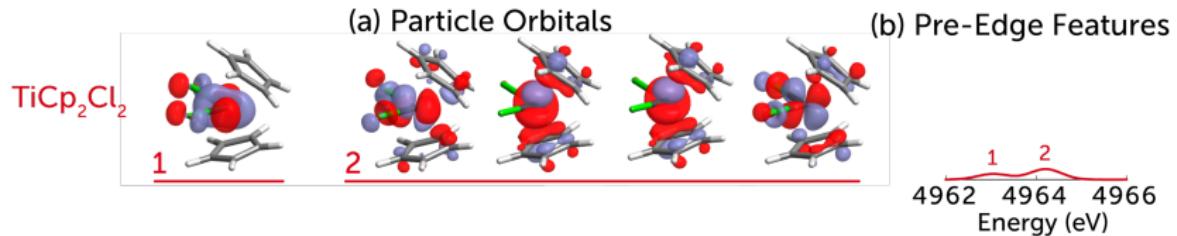
Particle Orbital Analysis of Pre-Edge TiCpCl_3



State	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 TiCp_2Cl_2



State	TiCp_2Cl_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

$$\mu_{0n} = \langle \Phi^{(n)} | \hat{\mathbf{r}} | \Phi^{(0)} \rangle = \sum_{\mu\nu} D_{\mu\nu}^{0n} \langle \chi_\mu | \hat{\mathbf{r}} | \chi_\nu \rangle \quad (20)$$

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

$$\mu_{0n}(A_{l_A} \rightarrow B_{l_B}) = \sum_{\mu \in A_{l_A}} \sum_{\nu \in B_{l_B}} D_{\mu\nu}^{0n} \langle \chi_\mu | \mathbf{r} | \chi_\nu \rangle \quad (21)$$

Further Investigation of Pre-Edge Intensity

Natural Population Analysis

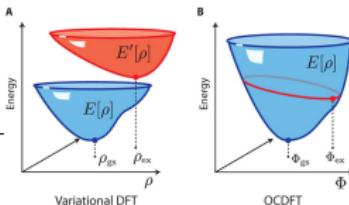
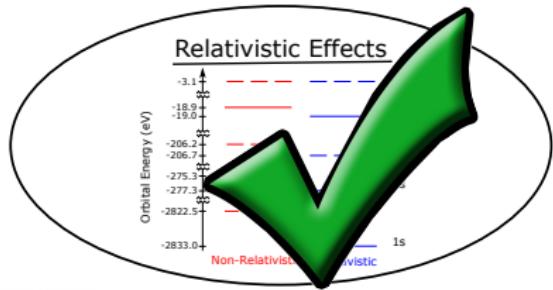
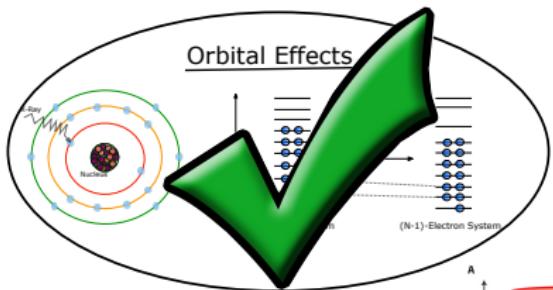
State	ΔTi_p			ΔCl_p			ΔTi_d		
	TiCl ₄	TiCpCl ₃	TiCp ₂ Cl ₂	TiCl ₄	TiCpCl ₃	TiCp ₂ Cl ₂	TiCl ₄	TiCpCl ₃	TiCp ₂ Cl ₂
1	0.0107	0.0066	0.0097	-0.2184	-0.0597	0.0051	1.1348	1.1614	1.2586

Atomic Decomposition of Dipole Moments

Contribution	μ_x	μ_y	μ_z	$ \mu $
State 1				
Ti _s → Ti _p	-0.000395	-0.000079	-0.000113	0.000418
Cl _p → Cl _p	+0.000062	+0.000012	+0.000018	0.000066
Ti _s → Cl _p	-0.000006	+0.000003	-0.000064	0.000064
Other	-0.000007	+0.000002	+0.000073	0.000073

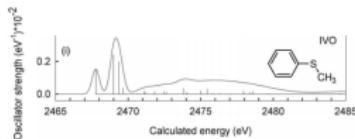
- Population analysis shows that the transitions are 1s → 3d
- Largest dipole contribution is Ti_s → Ti_d

Overview of Dissertation Work

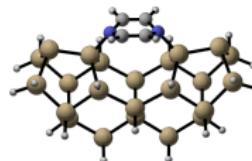


Orthogonality Constrained Density Functional Theory

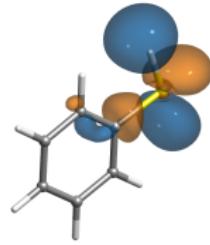
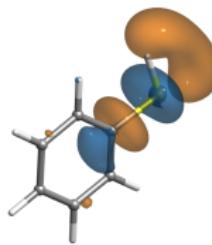
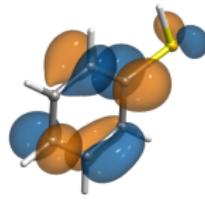
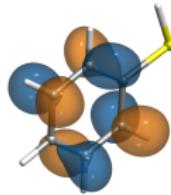
Assigning Transitions



Chemisorbed Complexes



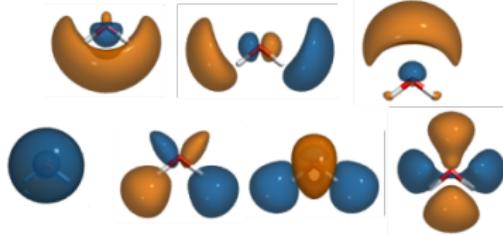
Assigning the Character of Particle Orbitals

 ϕ_p^1  ϕ_p^2  ϕ_p^3  ϕ_p^4

- ϕ_p^1 and ϕ_p^2 clearly have contributions from both σ_{S-C}^* and σ_{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 Intrinsic Valence Virtual Orbitals

(A) Canonical molecular orbitals (CMOs)

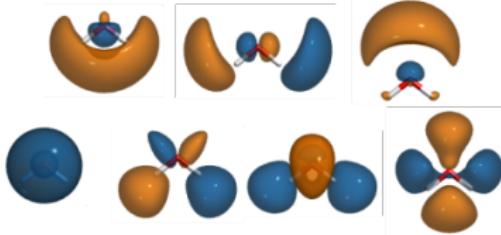


- Start with a set of virtual canonical molecular orbitals (CMOs) expanded in an atom-centered basis $\{\chi_\mu\}$

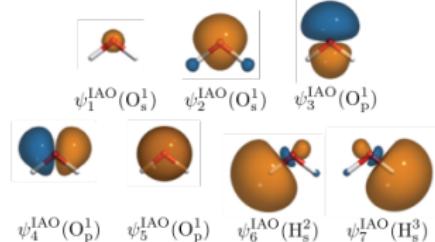
$$|\phi_a\rangle = \sum_{\mu}^{N_{AO}} |\chi_{\mu}\rangle C_{\mu a}, \quad a = 1, \dots, N_{vir} \quad (22)$$

Localized Intrinsic Valence Virtual Orbitals

(A) Canonical molecular orbitals (CMOs)



(B) Intrinsic atomic orbitals (IAOs)

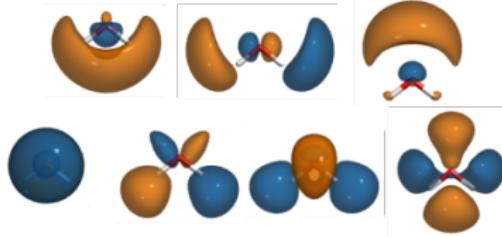


- Evaluate overlap (\mathbf{S}) with set of Intrinsic Atomic Orbitals (IAOs)

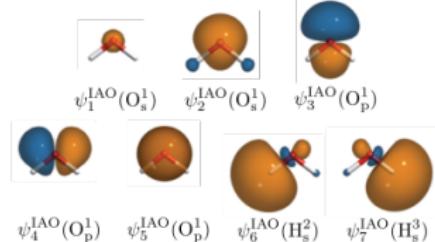
$$(\mathbf{S})_{a\rho} = \langle \phi_a | \psi_\rho^{\text{IAO}} \rangle \quad (23)$$

Localized Intrinsic Valence Virtual Orbitals

(A) Canonical molecular orbitals (CMOs)



(B) Intrinsic atomic orbitals (IAOs)

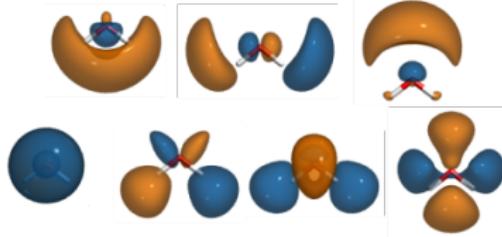


- Perform SVD of overlap matrix to get orthogonal transformation matrices \mathbf{U} and \mathbf{V}

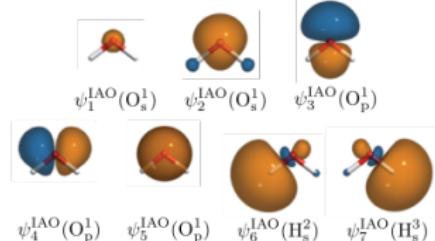
$$\mathbf{S} = \mathbf{U}\sigma\mathbf{V}^\dagger \quad (24)$$

Localized Intrinsic Valence Virtual Orbitals

(A) Canonical molecular orbitals (CMOs)

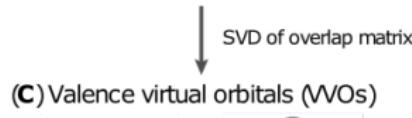


(B) Intrinsic atomic orbitals (IAOs)



LIMO Procedure

A) and (B)

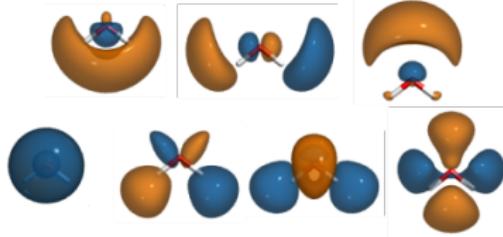


- Use \mathbf{U} to transform canonical virtuals into valence virtual orbitals (VVOs):

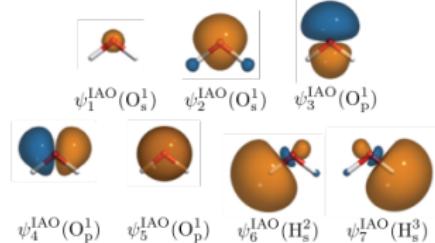
$$|\psi_v^{\text{VVO}}\rangle = \sum_a^{N_{\text{vir}}} |\phi_a\rangle U_{av}, \quad v = 1, \dots, N_{\text{VVO}}. \quad (25)$$

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

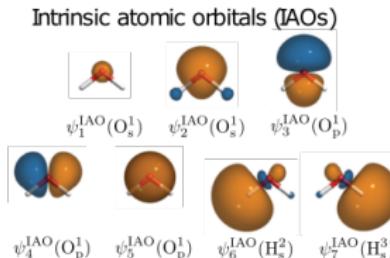
(D) Localized intrinsic WOs (LIVVOs)



- Pipek-Mezey localization can be employed in order to yield an orbital set that represents each valence antibonding interaction in the molecular environment

Determining Atomic Character of IAOs

- Atomic character is assigned using a Mulliken Population Analysis



Gross Populations

A_l	ψ_1^{IAO}	ψ_2^{IAO}	ψ_3^{IAO}	ψ_4^{IAO}	ψ_5^{IAO}	ψ_6^{IAO}	ψ_7^{IAO}
O_s^1	1.00	1.16	0.00	0.00	0.00	-0.08	-0.08
O_p^1	0.00	0.00	1.04	1.11	1.00	-0.07	-0.07
H_s^2	0.00	-0.08	-0.02	-0.05	0.00	1.18	-0.03
H_s^3	0.00	-0.08	-0.02	-0.05	0.00	-0.03	1.18

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

$$P_{\mu\nu}(\rho) = \tilde{C}_{\mu\rho} S_{\mu\nu} \tilde{C}_{\nu\rho}, \quad \rho = 1, \dots, N_{\text{IAO}} \quad (26)$$

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

$$\text{GP}_{A_l}(\rho) = \sum_{\mu \in A_l} \sum_{\nu}^{N_{\text{AO}}} P_{\mu\nu}(\rho) \quad (27)$$

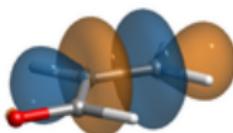
- character of each IAO chosen as maximum $\text{GP}_{A_l}(\rho)$ contribution

Using IAOs to Classify LIVVOs

- Overlap of each LIVVO (ψ_l^{LIVVO}) with the IAOs (ψ_ρ^{IAO}) is evaluated:

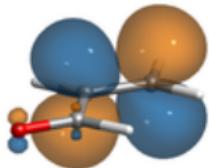
$$S'_{l\rho} = |\langle \psi_l^{\text{LIVVO}} | \psi_\rho^{\text{IAO}} \rangle|^2 \quad (28)$$

- Assign orbital character (σ, π, \dots) of LIVVOs based on atomic character (s,p, \dots) of IAOs



$$= 0.20 \psi^{\text{IAO}}(\text{C}_s^2) + 0.24 \psi^{\text{IAO}}(\text{C}_p^2)$$

$$+ 0.20 \psi^{\text{IAO}}(\text{C}_s^3) + 0.25 \psi^{\text{IAO}}(\text{C}_p^3) = \sigma_{\text{C}^2-\text{C}^3}^*$$

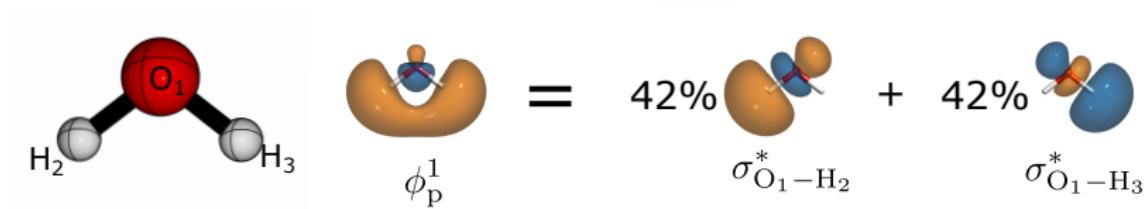


$$= 0.47 \psi^{\text{IAO}}(\text{C}_p^2) + 0.51 \psi^{\text{IAO}}(\text{C}_p^3) = \pi_{\text{C}^2-\text{C}^3}^*$$

Assigning Orbital Character of OCDFT Particle Orbitals

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

$$\Omega_{pl}^{(n)} = |\langle \phi_p^{(n)} | \psi_l^{\text{LIVVO}} \rangle|^2. \quad (29)$$

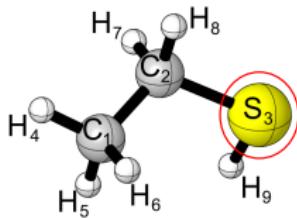


- Total valence character can be quantified by summing all LIVVO contributions. (84% for above H_2O example)

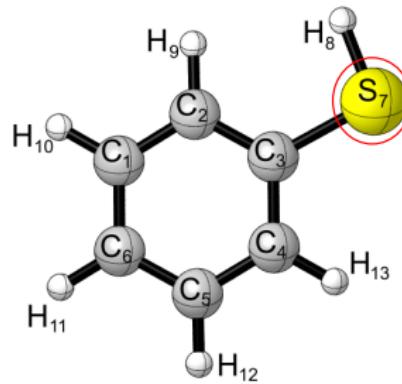
$$t_{\text{p}}^{\text{val},(n)} = \sum_l^{N_{\text{LIVVO}}} \Omega_{pl}^{(n)}. \quad (30)$$

Assigning Transitions in S K-edge of Ethanethiol and Benzenethiol

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

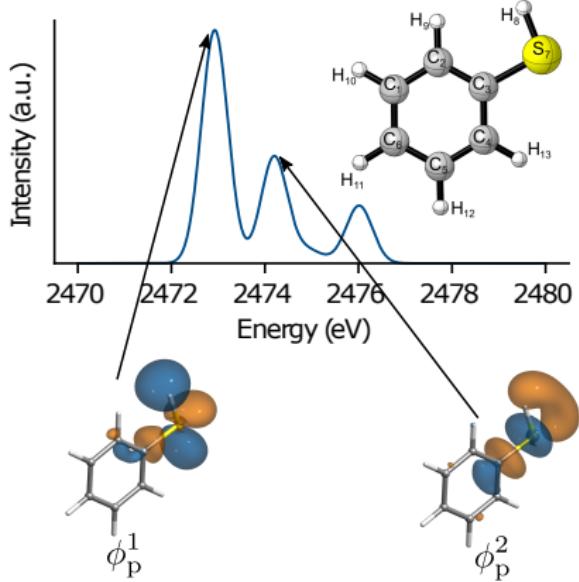
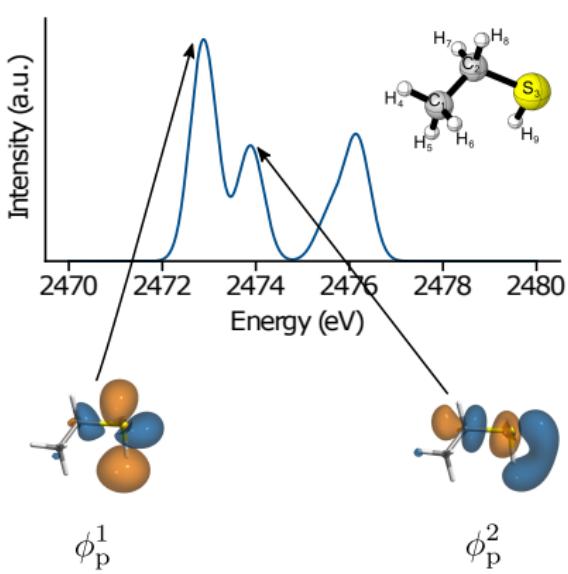


Ethanethiol



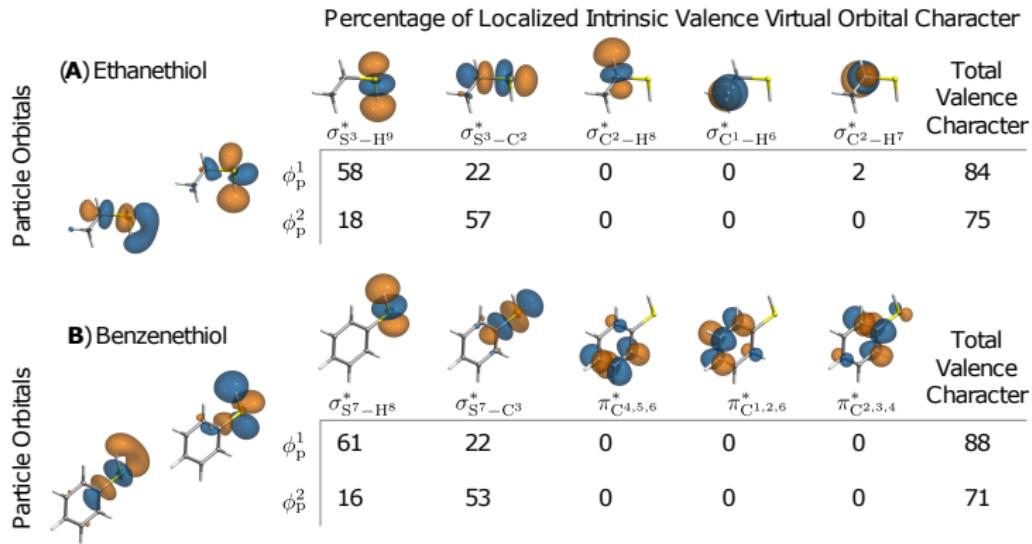
Benzenethiol

What are the local contributions to ϕ_p^1 and ϕ_p^2 ?



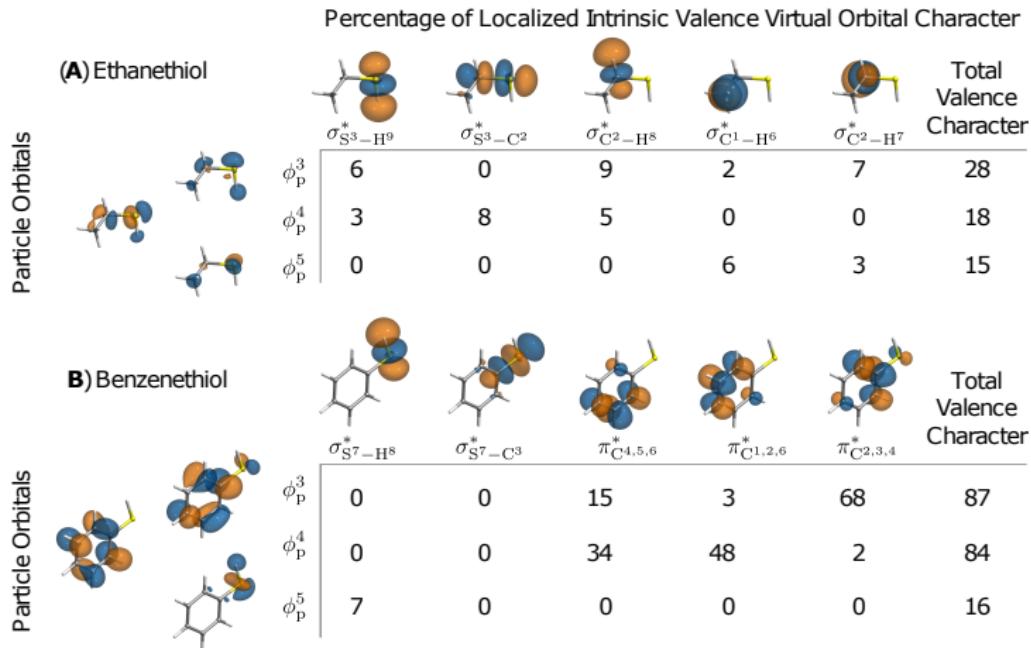
- Particle orbitals contain orbital character along S – C and S – H
- What is the contribution of the thiol bond to each excited state?

What are the local contributions to ϕ_p^1 and ϕ_p^2 ?



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

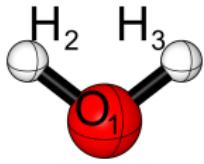
Other Contributions to the S K-Edge



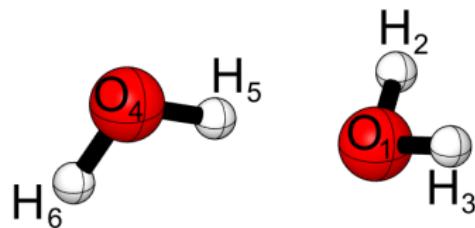
- ϕ_p^3 and ϕ_p^4 localized away from S atom in benzenethiol, results in lower intensity

Effect of Hydrogen Bonding on O K-Edge of Water

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

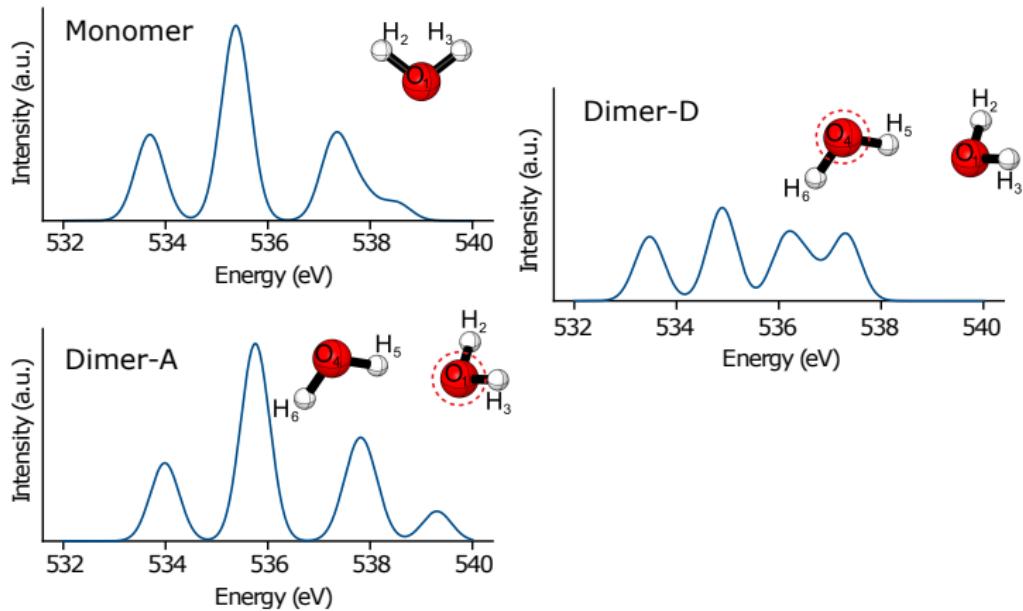


Monomer



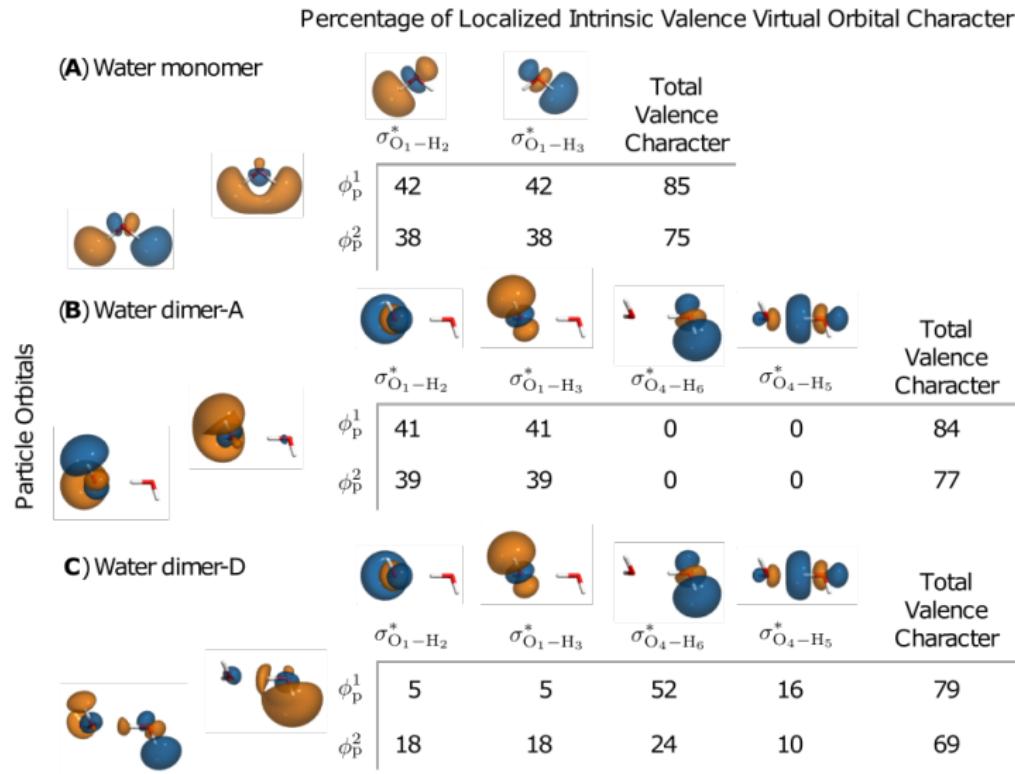
Dimer

Effect of Hydrogen Bonding on O K-Edge of Water

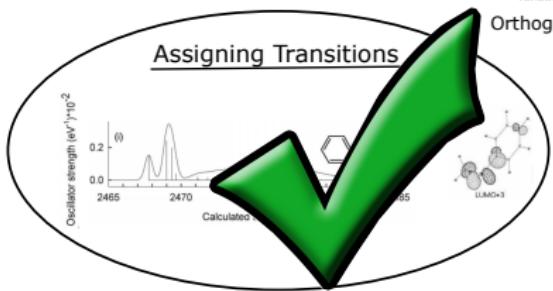
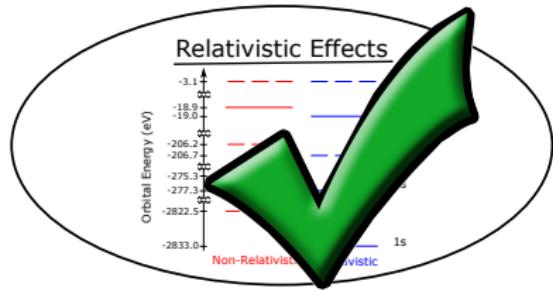
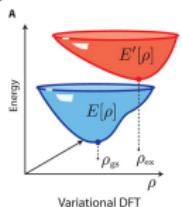
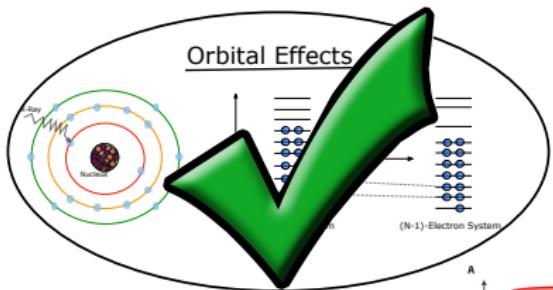


- Accepting H-bond (Dimer-A) has small effect on spectral features, donating H-bond (Dimer-D) has significant effect

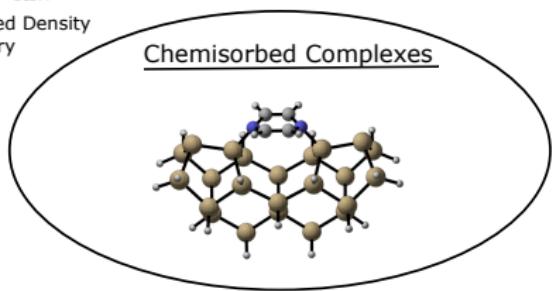
Effect of Hydrogen Bonding on O K-Edge of Water



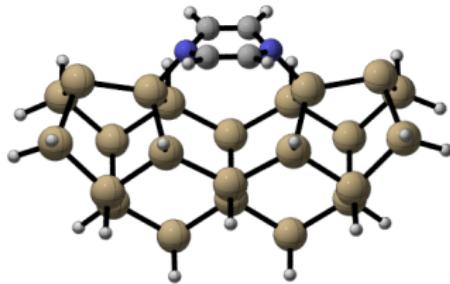
Overview of Dissertation Work



Orthogonality Constrained Density Functional Theory



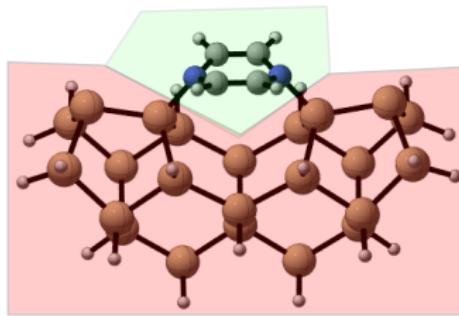
Organic Core-Excitations in Chemisorbed Molecules



Pyrazine ($C_4H_4N_2$) on Si(100)

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

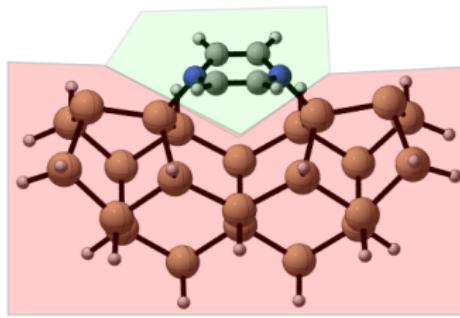
Organic Core-Excitations in Chemisorbed Molecules



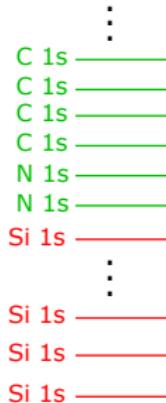
Pyrazine ($C_4H_4N_2$) on Si(100)

- 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)



- 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 (φ_s) ordered by atom center, principal quantum number, and angular momentum
- We can build an operator that spans a subset (s) of AOs

$$\hat{\Gamma}_s = \sum_s |\varphi_s\rangle\langle\varphi_s| \quad (31)$$

- Evaluate an atomic orbital occupation number (Ω_i) for each occupied molecular orbital (ϕ_i) within the desired subspace

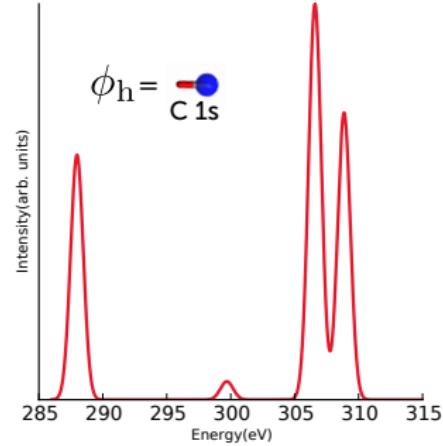
$$\Omega_i = \langle\phi_i|\hat{\Gamma}_s|\phi_i\rangle = \sum_s \langle\phi_i|\varphi_s\rangle\langle\varphi_s|\phi_i\rangle. \quad (32)$$

- Hole orbital (ϕ_h) is now chosen from a subset of the occupied orbitals where Ω_i is greater than a user-defined occupation threshold parameter

MSO-OCDFT: CO Example

	ϕ_i	Ω_i
5A ₁		0.008
1B ₂		0.000
1B ₁		0.000
4A ₁		0.008
3A ₁		0.007
2A ₁		0.976
1A ₁		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

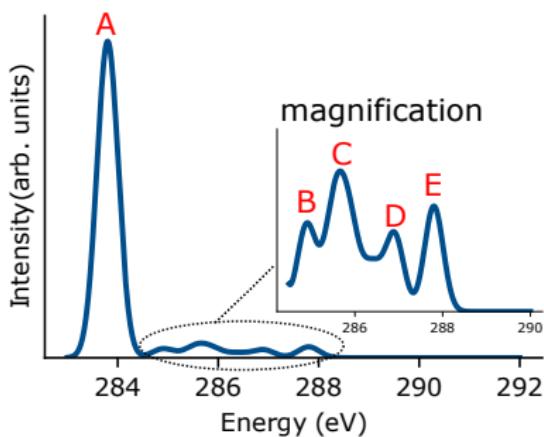
First 3 C core excitations in CCl_4

State	OCDFT		MSO-OCDFT	
	ω (eV)	f_{osc}	ω (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

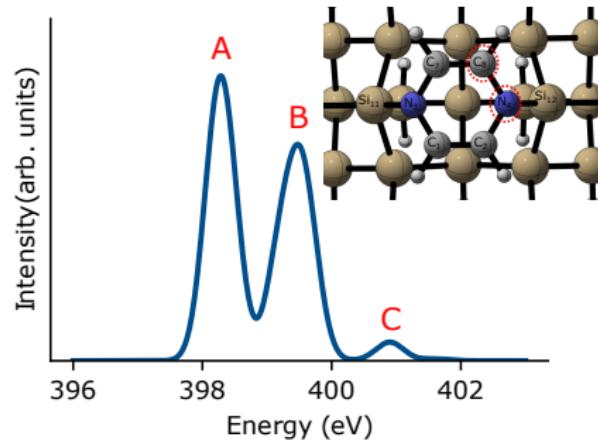
- Negligible differences between the two results
- Validates that this is a good approximation to full orthogonal set of solutions

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.

Professional Acknowledgments

Evangelista Lab Members



Francesco



York



Jeff



Sam



CiCi

Funding (\$\$\$!)



- ALL CURRENT EVANGELISTA GROUP MEMBERS! (Pictured above)
- Former Evangelista Lab Group Members
 - ▶ Dr. Prakash Verma
 - ▶ Kevin Hannon
- Funding from the NSF Graduate Research Fellowship Program
- Initial Funding from the NIH Initiative to Maximize Student Development (IMSD)

Family Acknowledgments



Charles
Derricotte Jr.
(Dad)



Glenda
Derricotte
(Mom)



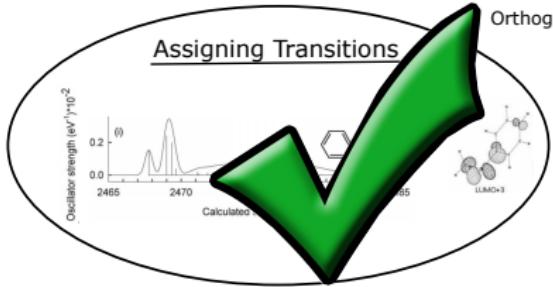
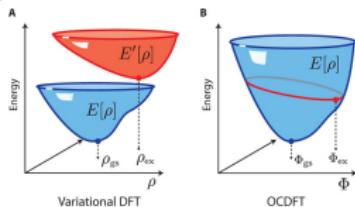
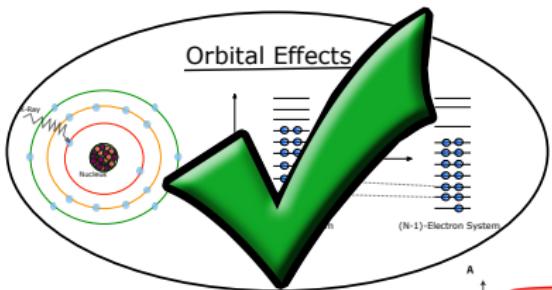
Alencia
Derricotte
(Wife)



Charles
Derricotte
(Brother)

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

Thank You!



Orthogonality Constrained Density Functional Theory

