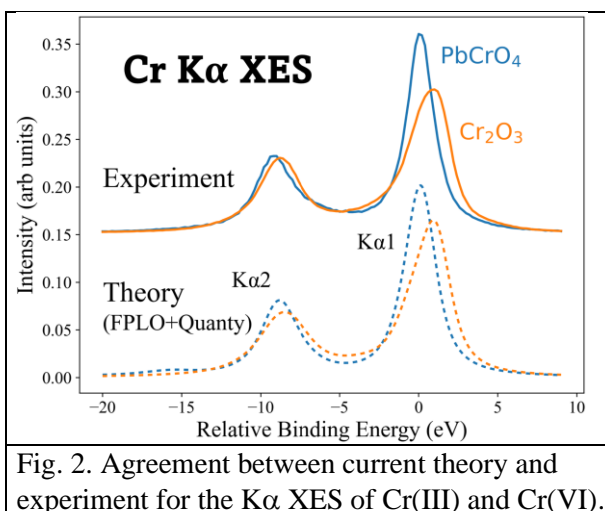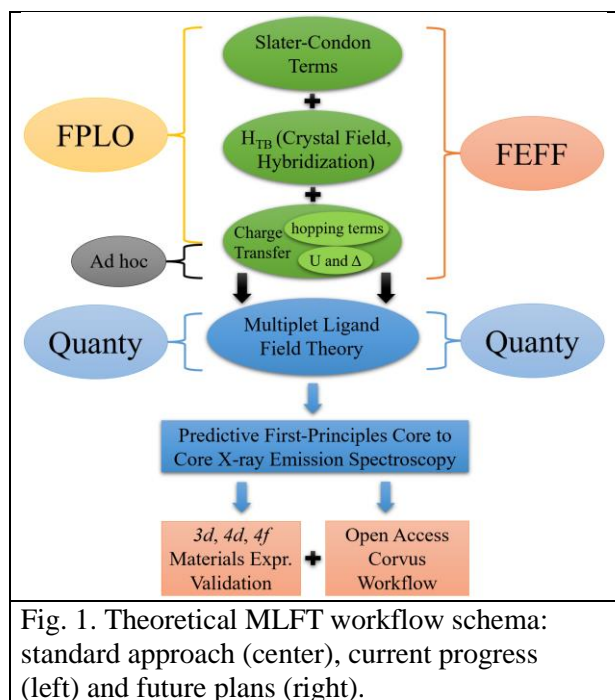**Objective**: Based on successful preliminary work, I will *develop*, *test*, and *deploy* a fully parameter-free, first-principles theoretical treatment of core-to-core x-ray emission spectroscopy (ctc-XES). Success in this research program will have wide impact for refining analytical and fundamental study of the element-specific electronic structure in highly correlated materials, an extremely broad class with significant industrial, technical, and environmental relevance. Furthermore, by having fully addressed the forward problem, i.e., prediction with no adjustable parameters of ctc-XES spectra from local structure, we will be able to use unsupervised and supervised machine learning (ML) methods to understand the information content in core-to-core XES across systems already widely studied (e.g., 3d transition metals) and also systems that have seem comparatively little XES (e.g., materials with heavy d- and f-electron elements). This will likely lead to prediction of new diagnostic spectral signatures of magnetism in f-electron systems.

Introduction and Background: X-ray emission spectroscopy (XES) is the very high-resolution study of fluorescence given off by the radiative decay of a core-shell excited atom, inherently probing the occupied electronic states. XES can carry information about the local chemical environment of the fluorescing atom, such as valence-level spin, oxidation state, ligand identity, local coordination geometry and bond covalency. While there are many truly first-principles theoretical tools for parameter-free calculation of most other advanced x-ray spectroscopies (e.g., XAFS, RIXS, and valence-to-core XES), the same is not true for ctc-XES, which is a deeply many-body problem where the treatment of highly correlated materials with partially filled *d*- or *f*- shells is especially challenging [1]. DFT approaches fail to describe the local many-body correlation effects while more accurate configuration interaction (CI) methods are computationally expensive and often difficult to implement beyond simple systems [1, 2]. Multiplet implementations are therefore the preferred theoretical framework for ctc-XES with many theoretical codes and models being developed over the last 40 years [3]. Those multiplet models show adequate agreement with experimental results *after fits to screening and correlation parameters*. Here, I will develop tools to calculate those parameters, ***moving from a <u>descriptive</u> treatment to a <u>predictive</u> treatment*** of ctc-XES.

Research Plan: My research plan has three main components: (1) A theoretical component that builds off of my prior work (below) and the expertise available from my theory mentors, Profs. Rehr and Kas; (2) Validation via measurement of ctc-XES across a wide range of materials, this capability is firmly enabled by lab-based XES available in my Ph.D. advisor's lab (Seidler group, UW); and (3) a ML component that will build on emergent methods in the XAS community, such as recent Seidler group work on unsupervised ML [6]. Hence, I am strongly supported by local expertise and needed facilities.

Beginning with theory, Figure 1 shows the distinction between common practice, the result of my work over the past six months, and a large part of the proposed further improvements. First, the central green column highlights the key-components that go into standard Multiplet Ligand Field Theory (MLFT). Note the need for many local environmental components such as the crystal field and charge transfer leads to a large increase in free parameters, limiting predictive capability. Next, the leftmost column shows my progress over the past 6 months building on work by Haverkort et al. [4] by applying a DFT + MLFT approach to ctc-XES, using the full-potential local-orbital (FPLO) DFT code to determine many, but not all parameters needed by the multiplet engine (Quanty). Using 'reasonable' values for the remaining undetermined parameters, I find excellent agreement between my new calculations and experiment for the environmentally important speciation of Cr^{3+} with respect to the carcinogenic Cr^{6+}, see Figure 2. Third, as shown in the right column of Figure 1, I will use the real-space Green's function code FEFF to both replace FPLO and also implement new calculation of the thus far undetermined parameters for the MLFT treatment [5]. The result will be the first truly parameter-free, first-principles MLFT treatment of ctc-XES.

Moving to experimental validation: past, ongoing, and recently funded work in the Seidler group includes ctc-XES measurements of numerous elements in battery materials, oxygen evolution reaction catalysis, cements used in long-term storage of toxic and radioactive wastes, and carcinogens occurring in consumer products or industrial wastes (e.g., Cr toxicity, such as probed by Figure 2). This provides a plethora of testing grounds across numerous problems with high societal relevance. In this work, I will be able to collaborate with other students in the group to design reference standard studies, validate against my theory calculations, and then apply the resulting information to draw best inferences about the systems of actual interest.

Fig. 1. Theoretical MLFT workflow schema: standard approach (center), current progress (left) and future plans (right).

Fig. 2. Agreement between current theory and experiment for the Kα XES of Cr(III) and Cr(VI).

Finally, the validated theoretical approach will be distributed to the general x-ray spectroscopy community via the workflow management tool Corvus and will also be used as the basis for ML investigations of the information content of ctc-XES. This latter work will start with unsupervised ML, such as t-SNE, which the Seidler group recently introduced as an important way to determine the chemical information content in vtc-XES and XANES [6]. This will be the first ML study of this kind to be applied to ctc-XES as traditional theory methods are either too inaccurate or too computationally expensive compared to the novel DFT+MLFT approach. This work will help determine which general problems are, or are not, well-encoded into ctc-XES across the periodic table and different chemical classes.

Intellectual Merit: The interleaved characterization of local atomic and electronic structure poses central challenges across numerous problems, including electrical energy storage, catalysis research, aging of construction materials, toxicity in consumer products, environmental consequences of industrial wastes, and low-diffusion matrices for long-term storage of toxic or radioactive wastes, all of which still have open questions that require an MLFT approach to accurately describe. These questions come at a time of rapid growth in access to experimental ctc-XES capabilities via the development of lab-based instrumentation for education and analytical study (a trend led by Seidler group), major upgrades of synchrotron facilities and specialized XES end-stations for applications in energy sciences, and the steadily increasing application of XES in ultrafast x-ray free element laser (XFEL) studies probing chemical and electronic dynamics.

This project will have a uniquely outsized impact not only because of the importance of the social and scientific problems being addressed but because of the synergy with the emerging experimental access to core-to-core XES capabilities. Additionally, the open access model of the tools developed in this research program will facilitate broad adoption within the x-ray community, bridging the gap between accurate *ab-initio* theoretical methods and the experimental need for reliable first-principles theory.

Broader Impacts: Much of my prior experience in outreach has centered around introducing people to a side of science which focuses on the curiosity and intrigue sparked by the natural world around us. I firmly believe that to accomplish this, access to intuitive introductory tools is a necessity. As addressed in my personal statement, I will continue to develop and refine x-ray specific educational material such as the XAS-RW, addressing the acute need for qualitative and intuition based introductory material in my subfield. I will compliment this with fun, science-based community engagement efforts through groups such as the UW Science Explorers and UW Stem Pals to bring hands-on physics directly into the classroom. This will provide the ideal environment to expand upon my Physics Field Day event, as I couple my organizational experience with new community collaborations to deliver a unique, immersive program.

Works Cited: *[1]doi:10.1002/qua.24905;[2]doi:10.1002/cphc.201800038;[3]doi:10.1016/j.elspec.2021.147061;[4]doi:10.1103/PhysRevB.85.165113;[5]doi:10.1039/B926434E;[6]doi:10.1039/D1CP02903G*