Determination of Hubbard U Magnitude and Magnetic State

The generalized gradient approximation can fail to describe systems with localized (strongly correlated) *f*-electrons. This is often remedied by applying a Hubbard-like term to treat the strong on-site Coulomb interaction, commonly referred to as DFT+U (also LDA+U or GGA+U) [1]. Determination of the appropriate magnitude of the applied screening needs to be uniquely determined for each element within each compound. The rotationally invariant approach of Dudarev [2] was implemented to investigate the effects of Coulombic screening, with the vdW-DF2 Van der Waals functional. The density, bandgap, and energy per molecule were analyzed as a function of U-J (Ueff) in increments of 1 eV for both UCl3 and NaCl-33UCl3 at 1250 K, in the ferromagnetic (FM) and anti-ferromagnetic (AFM) states.

The equilibrium density was determined by constructing pressure as a function of volume curves as a function of Ueff at 1250 K for both the FM and AFM states. As will be discussed later, there is not an exact correspondence between the AIMD predicted densities and the experimental densities, but reasonable agreement is achieved. There exists a general trend of decreasing density with increasing Ueff, and that the AFM state predicts a slightly higher density (lower volume) than the FM state. These equilibrium volumes are then utilized to determine the electronic density of states and the energy per molecule of their respective systems. A full discussion of densities is included in section X.X.

The electronic density of states of AFM UCl3 with a Ueff of 0 and 4 eV is shown in Fig X1. It can be seen that at a Ueff of 0 eV with no Coulombic screening, UCl3 exists electronically as a conductor. It is known that this molten salt exhibits insulating properties (need citation) with at least a minimal band gap. With the application of the Hubbard U term, an insulating electronic structure is induced, as can be seen in Fig. X1b. The magnitude of the bandgap changes as a function of the magnitude of Ueff, with no bandgap below 2 eV, and the bandgap progressively increasing up to approximately 2.3 eV for a Ueff of 5 eV. The magnitude of the bandgap of UCl3 has not been experimentally determined, removing the possibility of fitting the Ueff to the experimental bandgap.



Fig. X1. Density of states of UCl3 at 1250 K for a Ueff value of a) 0, and b) 4 eV.

The energy per molecule of UCl3 as a function of the magnitude of Ueff is shown in Fig. X1. It can be observed that the preferred magnetic state changes as a function of Ueff, with FM being preferred in the low Ueff/conducting region, and the AFM state preferred in the high Ueff/insulating region. It is theorized that at high temperatures one would not expect an ordered series of spins, and that is confirmed within this work, given that the electronic structure is appropriately accounted for. A previous study [3] investigated UCl3 in the FM state without DFT+U corrections. Although it was shown above that this incorrectly produces an electronically conductive molecular system, the choice of the FM state, given the absence of a Hubbard U term, is not wholly incorrect. For a Ueff value of 0, the FM state is the energetically preferred form of magnetism.



Fig. X1. Energy per molecule of UCl3 as a function of the magnitude of the Hubbard U term.

It is clear that a value of Ueff greater than 2 eV is required to ensure the proper insulating electronic structure, and that this system prefers an AFM state. However, the actual magnitude of the optimal Ueff value remains unclear. Thus, a further analysis on NaCl-33UCl3 was performed to observe what trends in the electronic structure and energy per molecule exist as a function of Ueff.

For the sake of brevity, a full description of results is not included. However, it was observed that at a Ueff value of greater than 1 eV, an insulating electronic structure was induced, while the absence of the Hubbard U term yielded a conducting system. Additionally, the AFM state becomes energetically favorable above a Ueff of 2 eV. The trends in the density fort NaCl-33UCl3 as a function of Ueff are statistically indistinguishable from those for UCl3. This investigation served to reinforce the findings that value of Ueff greater than 2 eV is required to ensure the proper insulating electronic structure, and that the NaCl-UCl3 system prefers an AFM state.

Additionally, the constrained DFT linear-response method [cite] was utilized within the Lichtenstein approach [cite] for the Hubbard U term of UCl3. An approximate U value range of 3.0-4.5 eV was determined and the J value was set to 0.51 eV. These values are similar to those proposed for UO2 [cite]. Given the lack of high-fidelity experimental data to serve as a basis for optimization of the Hubbard U magnitude, it was determined that a Ueff value of 4 eV (in the case of Dudarev) or a U value of 4.5 eV and a J value of 0.51 eV (in the case of Lichtenstein) should be utilized for the NaCl-UCl3 system

1. Rohrbach. <https://doi-org.prox.lib.ncsu.edu/10.1088/0953-8984/15/6/325>
2. Dudarev. <https://doi-org.prox.lib.ncsu.edu/10.1103/PhysRevB.57.1505>
3. Citation for UCl3 insulator
4. Li. DOI: 10.1021/acsaem.8b02157
5. Citation for Lichtenstein
6. Citation for UO2 U-J values