Ab Initio Multiconfigurational Dirac-Hartree-Fock Characteristic X-Ray Spectra

J.W. Dean, P. Pushkarna, H.A. Melia, T.V.B. Nguyen, and C.T. Chantler

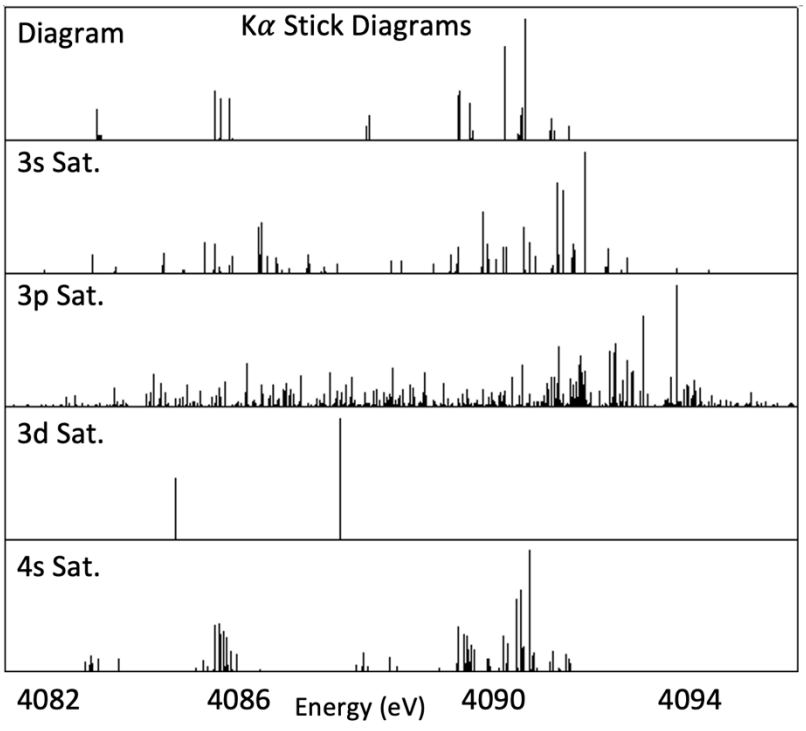
School of Physics, Melbourne University, Parkville, Victoria 3010, Australia.

A recent work by these authors has calculated the Kα and Kβ X-ray lines of scandium [1]. This represents a significant advancement in the field of theoretical atomic physics due to the complex nature of calculations involving open shell systems. Scandium has a lone 3d electron which greatly increases the number of configuration state functions that must be considered for a full basis set.

Prior to this work, there was a discrepancy of 0.549 eV between theory and experiment representing a 55σ discrepancy using the experimental uncertainty. This work improves this to a 0.330 eV discrepancy.

Calculating the X-ray transition line requires a multiconfigurational Dirac-Hartree-Fock approach using initial and final atomic state functions. The Kα/Kβ transitions arise when a 2p/3p electron from an excited atom with a 1s core vacancy. In terms of hole states this is represented by $[1s]^{-1} \rightarrow [2p]^{-1}$.

Asymmetries in these spectra were first noted by Siegbahn and Stenstrom in 1916 yet over one-hundred years later there is still active debate on their origin. The leading theory, which we show accounts for at least 80% of the asymmetry, are shake effects, first suggested by Wentzel in 1921. A shake event is when a secondary electron is *shaken* from the atom into the continuum during the initial ionisation. Then, the transition takes place under an altered potential resulting in energy shifts and satellite transition lines. For example, a Kα 3d shake-off satellite line is $[1s3d]^{-1} \rightarrow [2p3d]^{-1}$.



The end product of these calculations are sets of stick diagrams that show the eigenenergies of each transition. Due to electron coupling and hole states there are numerous eigenvalues. The stick diagrams for the Kα diagram line and 3s, 3p, 3d, 4s satellite lines are shown in the Figure.

Each stick represents the centroid and integrated intensity of a Lorentzian profile. A width is then fitted to the experimental data and goodness-of-fit measures are given which enables us to hypothesis test the theoretical underpinnings of the asymmetries in characteristic X-ray spectra.

[1] J. W. Dean, P. Pushkarna, **H. A. Melia**, T. V. B. Nguyen, C. T. Chantler, Theoretical calculation of characteristic radiation: multiconfiguration Dirac–Hartree–Fock calculations in scandium Kα and Kβ, J. Phys. B **55** (7) (2022) 075002. doi:10.1088/1361-6455/ac61ed.